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Composition and transport of sludge-derived organic carbon in soil and aquifer material

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Composition and transport of sludge-derived organic carbon in soil and aquifer material

by

Nizhou Han

A dissertation submitted to the graduate faculty

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Nizhou Han

has met the dissertation requirements of Iowa State University

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For the Graduate College

TABLE OF CONTENTS

GENERAL INTRODUCTION

Introduction

One of the great concerns about heavy application of sewage sludge on land has been the accumulation of heavy metals in soils and possible contamination of surface and ground water. The migration of metals in sludge-amended soils or shallow aquifers is closely related to the dissolved organic substances in the system because of their metal-binding reactions. A portion of the dissolved organic carbon (DOC) derived from applied sludge or sludge-amended soils could readily be flushed into shallow aquifers during storm events. Recently, soil- and stream-borne DOC has been evaluated extensively in terms of its mobility, interactions with the aquifer solid phase, and influence on mobility of certain metals. However, little comparable information is available involving sludge-derived DOC. In order to assure safe land disposal of municipal sewage sludge, the influence of sludge-derived DOC on metal mobility in shallow aquifers needs to be thoroughly studied, since soluble organic substances are abundant in sewage sludge.

The objectives of the present study were i) to characterize the DOC in sludge and sludge-amended soil, ii) to determine the Cu-binding ability and mobility of various DOC subcomponents in the sludge, and iii) to examine the influences of sludge-derived DOC on Cu-mobility in a shallow aquifer matrix.

Dissertation organization

In addition to the Literature Review, this dissertation includes three major parts. Part I deals with the effect of sludge application on the content and composition of soil DOC under two vegetation treatments. Part II emphasizes the Cu-binding ability of various

DOC subcomponents derived from a sewage sludge source. Part III, the main portion of the dissertation, addresses the mobilities of sludge-derived DOC subcomponents and their influences on Cu mobility in an aquifer material by using column experiments. The major findings and possible environmental implications are summarized in the General Conclusion.

Literature Review

The nature of dissolved organic carbon in sludge and sludge-amended soil

Dissolved organic carbon (DOC) refers to organic substances present in natural water or that may be extracted from soil or sludge by water or dilute neutral salts. In sludge and sludge-amended soil, DOC consists of a myriad of substances which are classified into three categories:

1) biochemical compounds
2) humified substances
3) artificial compounds

Biochemical compounds. Biochemical compounds are generated by decay of plant, animal and microbial tissue in their original or in a slightly modified forms. These include simple aliphatic acids, aromatic acids, amino acids, sugar acids, sugar amines, polyphenols, polysaccharides, proteins, pigments, hormones and so on (Holtzclaw et al., 1980; Tan, 1986; and Qualls and Haines, 1991). Simple biochemical compounds are subjective to rapid destruction by microorganisms and often assumed to be of little importance. However, these compounds are periodically produced in soil through microbial activity, and the amounts present in the soil solution will vary over time and will represent a balance between synthesis and destruction by microorganisms. High amounts are often

found in rhizospheres (Rovira, 1969), near decomposing plant residues (Bruckert, 1970), and in soils amended with sludge (Part I of the dissertationj).

Humified substances. Humified substances consist of a series of acidic, yellow- to black-colored polyelectrolytes. Fulvic acids (FAs) (soluble in base and acid), humic acids (HAs) (soluble in base and insoluble in acid), hymatomelanic acids as well as hydroxybenzoic acid derivatives derived from oxidative degradation of the humic substances are included in this category (Tan, 1986). Fulvic-acid-type substances have considerably lower molecular weights and higher total acidities than humic acids (Stevenson, 1994). Fulvic acids are less susceptible to precipitation with acids and polyvalent cations than HAs; thus they are the predominant form of humic substances in soil solutions and natural waters (T. A. Jackson, 1975; Dawson et al., 1978, 1981).

Fulvic acids are also believed to be the most important water-soluble, organic fraction of anaerobically digested sludge, in terms of their interactions with clay minerals and with metal cations in the soil solution in sludge-amended soils (Holtzclaw et al., 1976; Holtzclaw and Sposito, 1978). The studies of FAs extracted from anaerobically digested sludge have indicated that these substances are high in sulfur content and have low glucosamine / galactosamine ratios compared to soil-derived fulvic acids (Sposito et al., 1976; Holtzclaw et al., 1980). Holtzclaw et al. (1980) suggested that the high level of galactosamine in sludge-derived fulvic acids may be related to an abundance of anaerobic bacteria which contain this amino sugar and thrive during the sludge digestion process. Fulvic acids extracted from sludge-derived soils more resemble typical sludge-derived FAs than the FAs extracted from natural soil (Sposito et al., 1982). However, these FAs show a greater content of carboxyl and other titratable functional groups. This greater acidity is likely caused by the further oxidative decomposition of the sludge in amended soil (Sposito et al., 1982).

Artificial compounds. In sludge and sludge-amended soils, dissolved organics may include variety of human-made chemicals for domestic use. Of these chemicals, anionic surfactants (popular detergents) are compounds of environmental concern that may be present in significant quantities in sludge-amended soils (Acher and Yaron, 1977; Holtzclaw and Sposito, 1978). Anionic surfactants like linear alkyl sulfonate (LAS), dodecyl benzene sulfuric acid sodium salt (DDBS) and sodium lauryl sulfate (NaLS) are persistent in the soils in unaltered and partially biodegraded forms or incorporated into humic substances, contributing to the high sulfur content of sludge-amended soils (Holtzclaw and Sposito, 1978; Sposito et al., 1982).

Fractionation of dissolved organic carbon

Since DOC is a diverse mixture of organic compounds, including various biochemical compounds, humic substances and artificial chemicals, characterization of soil DOC is very difficult. Researchers fractionate DOC by several different approaches:

1) division into hydrophilic and hydrophobic subcomponents (Leenheer and Huffman, 1979; Leenheer, 1981)
2) molecular weight distribution (Collins et al., 1986; Homann and Grigal, 1992)
3) analysis of specific compounds or groups of compounds, e. g., organic acids and polyphenols (Pohlman and McColl, 1988)
4) analysis of functional groups, e. g., carboxyl, phenolic hydroxyl and amine groups (Sposito et al., 1982; Dahlgren and Ugolini, 1989).

The most logical approach in a study is dependent upon the motivation for characterizing the DOC and the equipment available. The hydrophilic / hydrophobic separation and molecular weight fractionation are used in the present study.

Dissolved organic carbon is often operationally fractionated into hydrophobic and hydrophilic subcomponents by chromatography using a nonpolar, nonionic, macroreticular Amberlite XAD-8 resin at a given ratio of resin to water eluent. Organic solutes that are sorbed on XAD-8 are termed hydrophobic, and organic solutes that are eluted are hydrophilic. Each of the subcomponents can be further separated into bases, acids, and neutrals (Leenheer and Hoffman, 1979; Leenheer, 1981). The hydrophobic subcomponent may consist of fulvic acids, humic acids, humic-bound amino acids and peptides, humic-bound carbohydrates, polyphenols, long-chain fatty acids, aromatic acids, hydrocarbons, phospholipids, etc. The hydrophilic subcomponent may contain humic-like substances with low molecular weight and high COOH / C ratio, non-humic-polysaccharides, simple organic acids, etc. (Qualls and Haines, 1991). Several studies have suggested that operationally fractionating DOC into hydrophobic / hydrophilic subcomponents allows us more accurately to predict the fate of DOC-mediated contaminants through soil and aquifer systems (Keefer et al., 1984; Jardine et al., 1989; Dunnivant et al., 1992).

Molecular weight is an inherent property of soluble organics, and the knowledge of molecular weight distribution is also important for understanding the organic behavior and function of DOC. For instance, both low-molecular-weight and high-molecular-weight organics are capable of complexing metal ions. High-molecular-weight organics can form strong metal complexes, and most of the metal complexes formed by low-molecular-weight compounds have moderate to low strength (Kuiters and Wulder, 1990). Molecular-weight differences may imply a difference in mobilities of different soluble organics as well as associated contaminants in soil and aquifer. However, little information is available in the literature.

Molecular weight fractionation can be accomplished by gel permeation chromatography (Berden and Berggren, 1990), ultrafiltration (Collins et al., 1986), or dialysis membranes (Homann and Grigal, 1992).

Adsorption of dissolved organic carbon by soil and aquifer material

Dissolved organic carbon can be adsorbed by solid phases through complex interactions in soil and aquifer material. Since DOC acts as a carrier for numerous organic and inorganic contaminants, adsorption of the DOC will impede the mobility of the associated contaminants. Also, adsorption of DOC could affect the properties of the underlying solid and present a surface with very different physicochemical properties (Hunter, 1980). For instance, adsorption of trace elements by hydrous oxides with an adsorbed organic film on the surface may be substantially different from the adsorption behavior observed on pure oxides (Murphy and Zachara, 1995). Thus, adsorption of DOC on aluminosilicate clays as well as oxides has become a topic of interest to many investigators in order to predict the fate of colloid- and DOC-mediated contaminant transport through surface and subsurface materials (Davis and Leckie, 1978; Davis, 1982; Jardine et al., 1989; and Baham and Sposito, 1994).

Jardine et al. (1989), who studied the adsorption of stream DOC by two soils, found that both crystalline and noncrystalline Fe oxides and hydroxides from the soils adsorbed 50-70 % of the total adsorbed DOC. Phyllosilicates in the < 2 μm clay fraction adsorbed the remaining DOC, with kaolinite exhibiting a larger adsorption capacity than illite. These investigators also observed a preferential adsorption of hydrophobic DOC (fractionated by XAD-8 chromatography) by the soils relative to hydrophilic DOC. A batch adsorption study of peat-derived DOC by pure Fe oxide powder and performed by Gu et al. (1995) indicated that, calculated on the basis of oxygen content, more of the hydrophilic DOC fraction was adsorbed than the hydrophobic fraction because interactions occurred primarily between O-containing functional groups of the DOC fractions and the Fe oxide surfaces. Davis and Gloor (1981) showed that the high-molecular-weight DOC fraction isolated from lake waters was strongly adsorbed on alumina surfaces but low-molecular weight DOC was weakly adsorbed.

The mechanisms by which DOC is adsorbed on mineral surfaces are not clearly understood due to the heterogeneity and complexity of DOC and solid phases. The major adsorption mechanisms may involve:

a) hydrogen bonding

b) Van der Waals interaction (Inoue and Wada, 1968)

c) anion exchange (Inoue and Wada, 1968; Jardine et al., 1989)

d) cation exchange

e) ligand exchange (Parfitt et al., 1977; Gu et al., 1994)

f) cation bridging

g) hydrophobic interaction (Jardine et al., 1989; Baham and Sposito, 1994)

Baham and Sposito (1994) argued that these mechanisms are hypothetical in that there are few direct microscopic measurements in the literature with which they can be evaluated.

The anion exchange mechanism refers to the formation of an "outer-sphere" complex between an organic anion and a protonated surface hydroxyl (OH_2^+) through weak electrostatic force. This mechanism is likely to be prominent only in acid soils whose clay fraction is comprised primarily of metal oxides. In the study of adsorption of DOC on allophane, Inoue and Wada (1968) believed that DOC was adsorbed on allophane through anion exchange.

Some of the organic compounds that contain functional groups, e.g., protonated amino groups or quaternary N in a heterocyclic aromatic ring, can be organic cations. These organic cations may displace exchange cations initially bound to a clay mineral surface through cation exchange (McBride, 1994).

Ligand exchange refers specifically to covalent bond formation between carboxyl / hydroxyl functional groups of DOC and Al or Fe oxide surfaces. Ligand exchange is distinguished from anion exchange by the high degree of specificity for sesquioxide

surfaces, a tendency to be nonreversible, a change in surface charge, and the release of OH^- ions. Gu et al. (1994) studied the adsorption of a wetland DOC on pure Fe oxide by measuring the heat of adsorption, by FTIR and ^{13}CNMR spectroscopy, and by competitive adsorption between DOC and some specifically adsorbed anions. They found that ligand exchange was the dominant adsorption mechanism, especially under acidic or slightly acidic pH conditions.

Cation bridging can be described by "the formation of a positively charged organic-metal complex that is then attracted to a negatively charged clay surface or conversely a negatively charged polymer is attracted to a clay colloid that bears positive charge from the adsorption of cations" (Baham and Sposito, 1994). The adsorption of humic and fulvic acids onto montmorillonite from aqueous solution has been found to be primarily attributed to cation-bridging, and the stability series followed $Ca^{2+} < Zn^{2+} < Cu^{2+} < Fe^{3+}$ (Theng, 1976). DOC molecules can also be adsorbed onto variable-charge mineral surfaces through cation bridging, in which the cations (particularly trace metal ions) are chemically adsorbed by the surface. McBride defines this type of cation bridging as a ternary complex formation (McBride, 1994).

Nonpolar DOC molecules may be adsorbed by the solid phase in soil or aquifer through hydrophobic interactions. Hydrophobic interaction refers to the enhanced adsorption of DOC in aqueous solution by the solid phase because the water-DOC interaction is weaker than the water-water interaction. The disruption of water structure by the hydrophobic surfaces of dissolved, nonpolar DOC molecules, particularly large ones, is energetically unfavorable. Consequently, nonpolar DOC molecules are forced out of solution and onto weakly hydrated surfaces of solid phases. Baham and Sposito (1994) studied the adsorption of DOC extracted from sludge by montmorillonite and kaolinite and concluded that hydrophobic interaction was the dominant adsorption mechanism, accompanied by an increase of configurational entropy.

Mobility of dissolved organic carbon in soil and aquifer material

Although DOC derived from various sources may be potentially adsorbed by solid phases, significant quantities of DOC in surface and subsurface soil materials are highly mobile and can be transported downward rapidly through the soil, particularly during large storms (Jardine et al., 1990). Using laboratory columns containing aquifer sediments, Dunnivant et al. (1992a) reported that different DOC subcomponents showed differences in the mobility. They determined that the hydrophilic subcomponent was more mobile relative to the hydrophobic subcomponent because hydrophobic DOC has a greater tendency to be adsorbed by the solid phase. A similar study of DOC transport was reported at the field scale (McCarthy et al., 1993). McCarthy et al. (1993) found that smaller (<3000 daltons) and more hydrophilic subcomponents of DOC were more mobile than were larger (3000-100,000 daltons), more hydrophobic components. The soil acidity, solid phase composition, and solution ionic strength are also important in controlling the mobility of different DOC subcomponents. For instance, Vance and David (1989) found that acidification facilitated hydrophilic DOC transport and retarded the mobility of hydrophobic DOC in a forested soil. They also observed a decrease in DOC movement with increasing ionic strength of the soil solution.

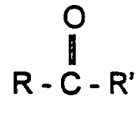
The difference in the mobility of different DOC subcomponents may indicate their potential roles in transport of organic or inorganic contaminants. Dunnivant et al. (1992a) argued that the more mobile hydrophilic subcomponents of DOC may be effective in facilitating the transport of some toxic metals and radionuclides. And the presence of hydrophobic subcomponents in a mobile phase may significantly accelerate the transport of organic contaminants. Unfortunately, relatively little information is available in the literature concerning these possibilities.

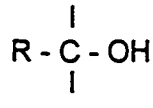
Complexation of DOC with heavy metal ions

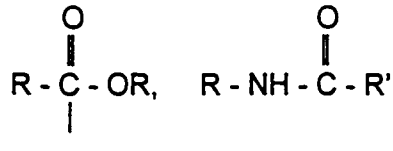
Functional groups. The metal-binding abilities of dissolved organic compounds are related to the presence of ligand atoms in their functional groups, e.g., oxygen atoms in carboxylic groups, nitrogen atoms in amine groups and sulfur atoms in sulfydryl groups. Modern analytical techniques (e.g., IR, NMR, and ESR) demonstrate that a metal ion (Lewis acid) is bound to an organic ligand (Lewis base) by sharing the electron pair supplied by the ligand atom. Dissolved organics extracted from sludge and sludge-amended soils have been found to be rich in various electron-donating functional groups (Sposito and Holtzclaw, 1977; Baham et al., 1978; and Dudley et al., 1987), including

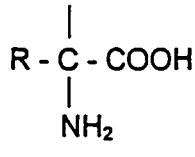
carboxylic R-COOH

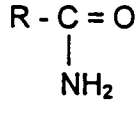
phenolic  -OH

ketone 

alcohol 

carbonyl 

amino 

amide 

amine $R-NH_2$, R_2NH, R_3N

sulphydryl R - SH

sulfonate R - SO_3^-

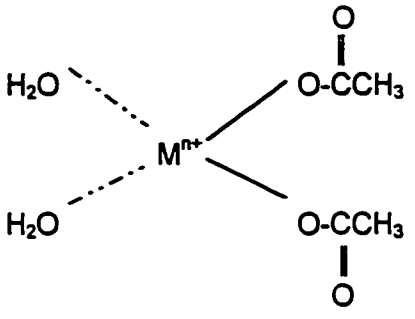
phosphate R - O - PO_3^{2-}

These functional groups are capable of interacting with metal ions, but their relative contributions to metal binding are difficult to estimate due to the complexity of such a chemically heterogeneous system. As for DOC in soil solution and natural waters, carboxylic and phenolic groups probably are important binding groups. Unlike DOC in natural water system, sludge-derived DOC is abundant in proteinaceous material (including amino acids) and organic sulfonates (Holtzclaw et al., 1980; Holtzclaw and Sposito, 1978). The N-containing and S-containing groups within the structures of these substances are expected to figure directly in complexation reactions with trace metals. For instance, Baham et al. (1978) found that -COOH and -SO_3H functional groups of sludge-derived DOC were responsible for metal binding, particularly for Cu binding, while Dudley et al. (1987) and Boyd et al. (1979) believed that Cu was associated primarily with amide functional groups of soluble organic compounds in sludge-amended soils.

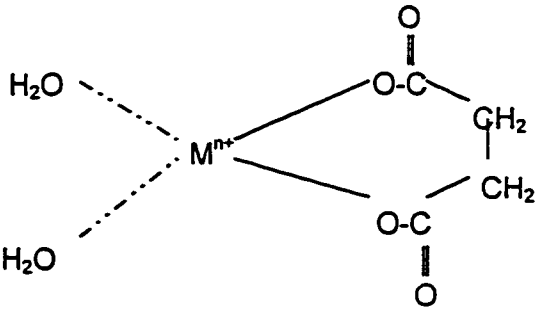
Mechanisms of complexation The mechanisms of that bind metal ions to organic ligands in soils have been studied for decades by various means (e.g., IR, NMR, and ESR). Owing to the complexity of soil organic ligands, some of the mechanisms are only postulated.

Monodentate ligands that have only one point of attachment to a metal ion react with metal ions to form a ligand-metal complex, e.g., the diaquodiacetate metal complex (I). Polydentate ligands that have more than one donor atom are capable of occupying several sites in a complex. They may surround the central metal ion similar to the claws to a crab surrounding its victim. Such complexes are referred to chelates,e.g., the diaquosuccinate metal chelate (II). Complexes containing several central atoms (metal ions) are termed

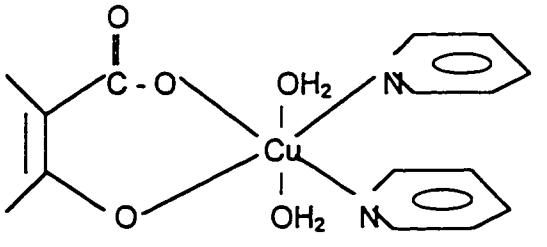
multinuclear complexes, and if ligands from more than one molecule are bound to a metal in one complex, the configuration is referred to as a mixed-ligand complex (e.g., III).



I Diaquodiacetate metal complex



II Diaquosuccinate metal chelate

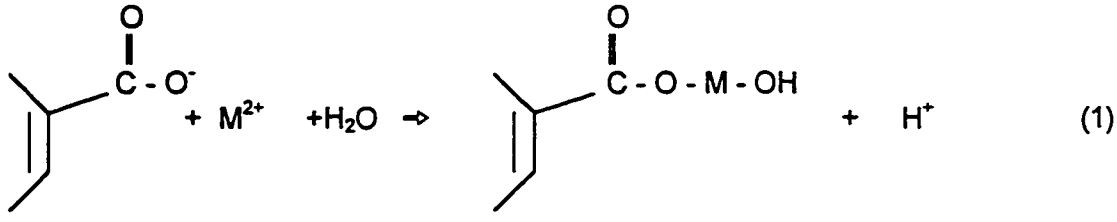


III. mixed-ligand complex

The terms chelates and complexes are sometimes used interchangeably by authors in the soil science literature. However, in a very dilute solution (e.g., pore water of soils), complexes even with quite high stability constants will dissociate to certain extent, while the corresponding chelate compounds are maintained without appreciable dissociation. The stabilizing effect of chelation increases rapidly with the number of metal chelate rings present (Martell, 1971). Complexation and chelation reactions between metal ions and

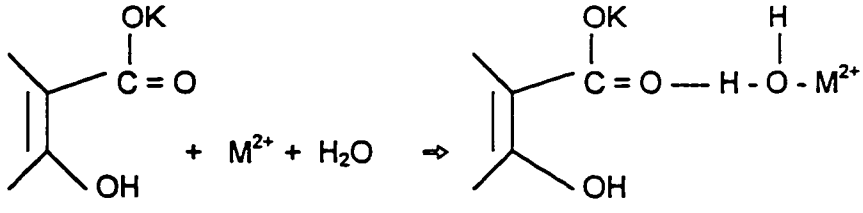
various ligands proceed by many different mechanisms. Some of the reaction mechanisms reported in the literature are discussed breifly as the following:

Inner-sphere complex



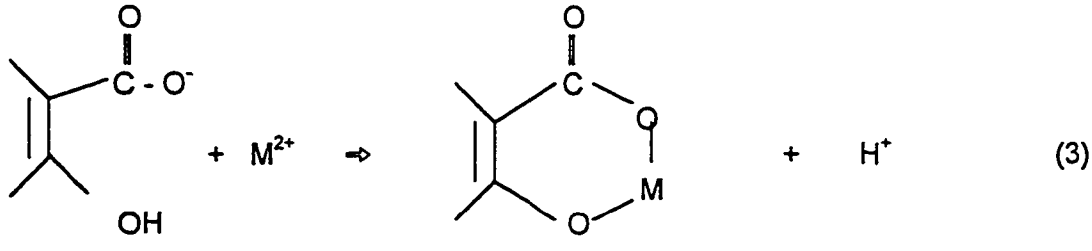
(1)

Outer-sphere complex



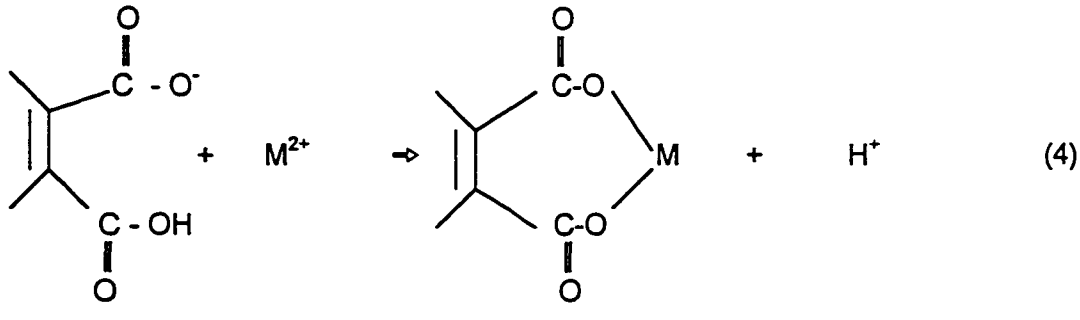
(2)

Salicylate-type chelation



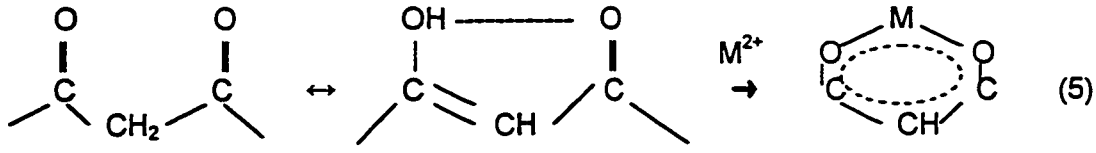
(3)

Phthalate-type chelation



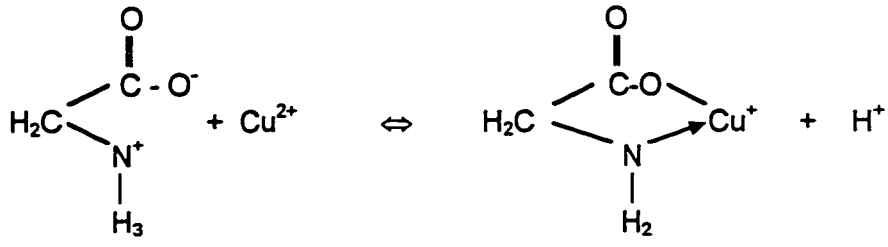
(4)

Conjugated ketonic-type chelation



(5)

Amino acid-type chelation



(6)

In reaction (1), one -COO^- group reacts with one metal ion to form a monodentate complex. In equation (2), the hydrated metal ion is bound to a ligand through a H bond between a water molecule in its hydration shell and - C=O group in the ligand, and a weaker outer-sphere complex is formed (Schnitzer, 1986). One -COOH and one adjacent phenolic - OH group in salicylic acids can react simultaneously with a metal ion to form a chelate, and two adjacent - COOH groups in phthalic acids interact simultaneously with a metal ion to also form a bidentate chelate (eq. (3) and (4)) (Cunningham, 1990). It is believed that humified organic acids contain both salicylic acid-like and *o*-phthalic acid-like segments (Stevenson, 1979; Schnitzer, 1986) and are capable of interacting with metals and forming salicylate-like and phthalate-like ring structures (Schnitzer,1969; Gamble et al., 1970; and Boyd et al., 1981). Schnitzer (1969) and Gamble et al. (1970) concluded that in metal-fulvic acid interactions the salicylate-type reactions are more important than the phthalate type. An infrared spectroscopic study showed that conjugated ketonic structures may form chelates with transition metal ions like Cu^{2+} and the formed chelates can be stabilized by the resonance effect (eq (5)) (Piccolo and Stevenson, 1982). The amino and carboxylate groups of an amino acid are also capable of chelating metal ions. The chelation of Cu^{2+} and glycine in eq. (6) was suggested by Avakyan (1971).

Stability constant (K). Stability constants are important characteristics of a metal-organic complex and provides a quantitative measure of the affinity of the metal (M) for the ligand (L):

$$aM + bL \Rightarrow ML$$

$$K = (ML) / (M)^a (L)^b$$

where a is the number of moles of metal ion complexed and b is the number of moles of organic ligands. The terms M, L, and ML denote molar concentrations of free metal, free ligand and the complex, respectively. Unfortunately, for uncharacterized DOC, it is not possible to express the concentrations of the organic ligands in molar units, and the concentrations of binding sites are often used instead. The determination of stability constants for metal-organic complxes is very difficult, since stability depends on a number of factors, including

a) the chemical nature of the metal ions (e.g., ionic radius and electronegativity); the chemical nature of the organic ligands (e.g., heterogeneous sites and chelation / complexation reactions);

c) the pH and ionic strength at which complexation is measured (this determines intensity of competition by H^+ and other cations for the complexing sites);

d) approaches for determining stability constant (e.g., potentiometric titration and ion-exchange).

Thus, Stevenson (1982) pointed out that stability constants obtained by various approaches are empirical at best. He has summarized the stability constants of Cu complexes with various source fulvic acids reported in the literature, and a simplified version of his summary is shown in Table 1. It can be seen that the stability constants of Cu-FA complexes varied with source and pH. Also, fulvic acids possess two types of binding sites, with one showing a greater affinity for Cu^{2+} than the other. Due to numerous

Table 1. Stability constants of Cu^{2+} complexes with FAs

Modified from Stevenson (1982)

FA sources	pH	Supporting electrolyte	log K Type 1	log K Type 2
water	8.0	0.01 M NaCl	8.80	8.05
water	6.0	0.01 M KNO_3	6.11	3.85
soil	5.0	Ibid	6.00	4.08
soil	4.0	0.1M $KClO_4$	5.60	3.95
sewage	5.0	0.1 M $KClO_4$	3.85	2.09

problems encountered in determining stability constants of metal-organic ligand complexes further research is needed in this area.

Maximum binding capacity (Xm). The maximum amount of metal ion that can be bound to dissolved organics is an indication of the content of functional groups of the ligands. Early studies on determination of the maximum binding capacity of various natural organic ligands were often accomplished by proton release (e.g., Stevenson, 1976; Stevenson, 1977) and metal ion retention as determined by competition with a cation exchange resin (e.g., Zunino et al., 1972; Crosser and Allen, 1977). The disadvantage of proton release method is that, at high metal / ligand ratio and / or high system pH, the H^+ may be released from hydration water of the metal ion instead of being released from metal-binding sites. The cation exchange resin approach requires much higher metal concentrations than ligand concentrations, i.e., concentrations which may not be relevant to metal concentrations observed in soil or aquifer environments.

Fitch et al. (1986) observed a Langmuir-type response when studying the Cu^{2+} ion binding-capacity of soil humic acids by ion selective electrode approach. Zunino and Martin (1977) were also able to estimate the maximum adsorption of Cu^{2+} onto microbial

polymers by fitting the Langmuir model. The Langmuir model provides a practical tool to estimate maximum binding capacity, Xm. The Langmuir equation is written as follows:

$$\frac{X}{Xm} = \frac{bC}{1 + bC}$$

where

X = Cu-complexed per unit mass of substrate

C = Cu^{2+} concentration in liquid phase at equilibrium

b = a constant indicating the affinity between Cu and the ligand

Xm = maximum binding capacity.

The Langmuir equation can be linearized, and the maximum binding capacity and the binding affinity can be calculated from the slope and the intercept of the line. It should be pointed out that original Langmuir equation is based on the assumptions that there is only a single layer of binding sites and that the bonding energy of all the sites is uniform and does not change with surface covering. However, the bonding energy of all sites is not uniform and does vary as complexation reaction goes on, particularly for macromolecules. Zunino and Martin (1977) placed the functional groups of organic ligands into three categories:

A. functional groups forming a chelate configuration — high level of bonding energy,

B. functional groups forming open complexes — intermediate level of bonding energy,

C. functional groups which are "buried" within the macromolecules are not highly accessible to the metal ion — low level of bonding energy.

It is believed that at low metal saturation the sites with high bonding energy would be preferentially occupied, and the sites with low bonding energy would be saturated only at relatively high metal concentrations. The energy-bonding term (i.e., b) calculated from the linearized equation might be some average value among all the sites.

Furthermore, the single layer of binding sites is difficult to define for organic ligands, particularly for the soluble organics. The use of the Langmuir model to estimate maximum binding capacity and binding energy is practical but empirical.

The determination of metal binding ability is influenced by the concentrations of metal ions and ligand, pH, ionic strength and so on. Therefore, measurement conditions need to be specified before comparision are made.

Effect of DOC on the adsorption of Cu by soil and aquifer material

Land application of sewage sludge and farmyard manure as a fertilizer, organic soil conditioner, or as a means of disposal has been a very common practice in the United States and many other countries in the world. Heavy metal concentrations in various sludges may exceed concentrations in unamended soil by two orders of magnitude or more (Table 2). The concentrations of Cu, Cr, and Zn can reach as high as 8,000, 40,600 and 49,000 μg / g soil, respectively. Various farmyard manures may also contain high concentrations of Cu and As that are fed to improve feed conversion efficiency (Table 2). The prospect of a significant increase in the concentrations of potentially harmful heavy metals in soil solution because of the application of sludge on land has stimulated research on the chemistry of heavy metal interactions with the organic components of sludge and inorganic constituents of soil.

Among common heavy metals, Cu in sludge is commonly abundant and often the first element to limit land application (McBride, 1994). Also, under many conditions Cu^{2+} is bound to many organic compounds more tightly than any other divalent transition metal

Table 2. Typical ranges of heavy metal concentrations (μg / g) in soil, sewage sludge, fertilizers and farmyard manures. From Alloway (1990).

	Soil	Sewage sludge	Phosphate fertilizers	Nitrate fertilizers	Farmyard manure	Composted refuse
Ag	0.01-8	<960	-	-	-	-
As	0.1-50	3-30	2-1200	2.2-120	3-25	2-52
B	-	15-1000	5-115	-	0.3-0.6	-
Cd	0.01-2.4	<1-3410	0.1-170	0.05-8.5	0.1-0.8	0.01-100
Co	1-40	1-260	1-12	5.4-12	0.3-24	-
Cr	5-1500	8-40,600	66-245	3.2-19	1.1-55	1.8-410
Cu	2-250	50-8000	1-300	-	2-172	13-3580
Hg	0.01-0.3	0.1-55	0.01-1.2	0.3-2.9	0.01-0.36	0.09-21
Mn	20-10,000	60-3900	40-2000	-	30-969	-
Mo	0.2-5	1-40	0.1-60	1-7	0.05-3	-
Ni	2-1000	6-5300	7-38	7-37	2.1-30	0.9-279
Pb	2-300	29-3600	7-225	2-27	1.1-27	1.3-2240
Sb	0.05-260	3-44	<100	-	-	-
Se	0.01-2	1-10	0.5-25	-	2.4	-
U	0.7-9	-	30-300	-	-	-
V	0.5-83	20-400	2-1600	-	-	-
Zn	10-300	91-49,000	50-1450	1-42	15-566	82-5894

(McBride, 1994). Thus, Cu was chosen as an indicator metal in DOC-metal and DOC-metal-clay interactions for the present study. The following review is mainly given to the effect of DOC on Cu adsorption by soil.

Cu adsorption in soil and aquifer material. Studies show that Cu is strongly adsorbed by individual components present in the soil solid phase, including aluminosilicate clays, oxides and hydroxides of Fe and Mn, as well as organic matter (McLaren and Crawford, 1973; Cavallaro and McBride, 1984; and Bibak, 1994). Isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheets and Fe^{2+} for Al^{3+} in the octahedral sheets results in the aluminosilicate clays having a net negative charge. Counterions such as K^+ and Ca^{2+} can undergo ion exchange with heavy metals like Cu^{2+} in solution:

$$2K\text{-}Clay + Cu^{2+}_{(aq)} \Leftrightarrow Cu\text{-}Clay + 2K^{+}_{(aq)}$$

Negatively charged humic material and oxides (when pH > PZC) may also possess cation-exchange properties (Guy et al., 1975). Amorphous aluminosilicates (e.g., allophanes), oxides and hydroxides of Fe, Al, and Mn, and even the edges of layer silicate clays to a lesser extent, provide surface sites for the chemisorption of transition and heavy metals. These minerals generate the adsorptive sites through adsorption of protons and hydroxyl ions:

$$>S\text{-}OH\,]^{-1/2} \underset{+OH^-}{\overset{+H^+}{\Leftrightarrow}} >S\text{-}OH_2]^{+1/2}$$

For example, chemisorption of Cu^{2+} by Fe oxides can be written (McBride, 1994):

$$>Fe\text{-}OH\,]^{-1/2} + Cu(H_2O)_6^{2+} \Rightarrow Fe\text{-}O\text{-}Cu\,(H_2O)_5]^{+1/2} + H_3O^+$$

The distinguishing features of chemisorption are the release of protons and an increase in surface positive charges.

Cu adsorption by soil and its components can often be described by the Langmuir model. McLaren and Crawford (1973) observed that the maximum adsorption capacity

estimated from the Langmuir equation for soil constituents followed the order manganese oxides > organic matter > iron oxides > aluminosilicate clays. A similar trend was also reported by Guy et al. (1975). Although aluminosilicate clays and iron oxides show less adsorption of Cu, in soil and shallow aquifers where they are abundant, their gross binding capacity may override that of organic matter and free manganese oxides.

Effect of DOC on Cu adsorption. The influence of DOC on metal adsorption is complicated and contradictory. Inskeep and Baham (1983) found that DOC stabilized Cu in soluble form and decreased Cu adsorption by Na-montmorillonite. O'Connor et al. (1983) also observed a decrease in Ni and Zn sorption in sludge-amended soils as the result of organic - metal complexation. On the other hand, the presence of DOC may enhance Cu adsorption by clay and oxide surfaces due to the formation of ternary complexes (Davis and Leckie, 1978 and 1979; Dalang et al., 1984; Petruzzelli et al., 1994). For instance, Petruzzelli et al. (1994) demonstrated a greater affinity of a sandy soil for Cu in presence of DOC extracted from sewage sludge.

Actual trends of the effect of DOC on Cu adsorption may depend on the types of ligands and on the solid surface present. By studying the effect of well-defined ligands on Cu^{2+} adsorption by amorphous $Fe(OH)_3$, Davis and Leckie (1978) observed either stabilization of Cu in solution by formation of nonadsorbable complexes or an increase in adsorption due to the ligands acting as bridges between the surface and the metal ion, depending on the configuration of the functional groups. For example, picolinic acid and 2,3-pyrazinedicarboxylic acid (2,3-PDCA), used in their study, have similar functional groups for metal complexation and comparable adsorption behavior by the solid surface. Picolinic acid effectively decreased Cu sorption to the solid phase, while 2,3-PDCA enhanced the adsorption of Cu. Davis and Leckie (1978) proposed that the surface bonding of picolinic acid involves donor electrons of the carboxyl group and nitrogen atom in heterocyclic rings (Fig. 1). Consequently, an adsorbed picolinate ion is not capable of

functioning as a complexing ligand for Cu, since the coordinating groups are blocked. Copper ion adsorption by the Fe oxide is decreased by complexation with the picolinate remaining in solution, as compared to the ligand-free system. However, adsorption of 2,3-PDCA by the solid surface leaves a strongly complexing functional group directed outward toward the solution (Fig. 1). This functional group may serve as a "new adsorption site" for trace metals at the surface or may stabilize metal ions sorbed at adjacent surface sites, as suggested by the ternary complex model (Type III, below).

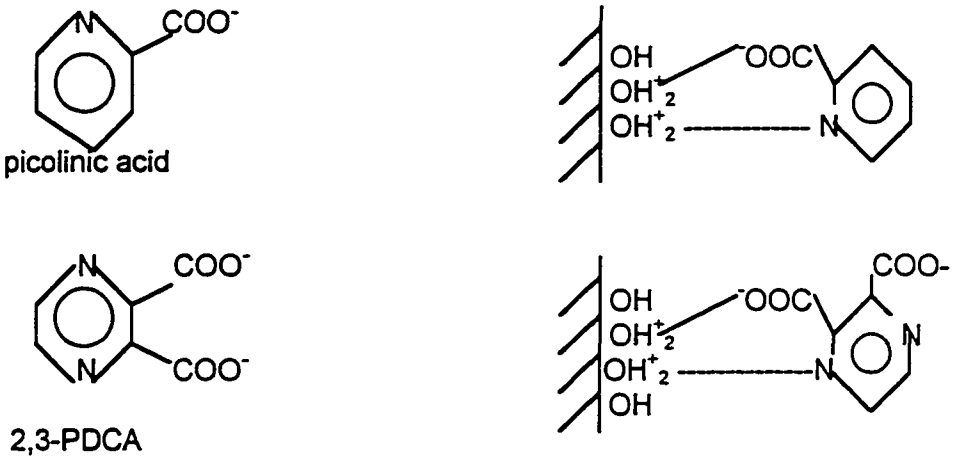
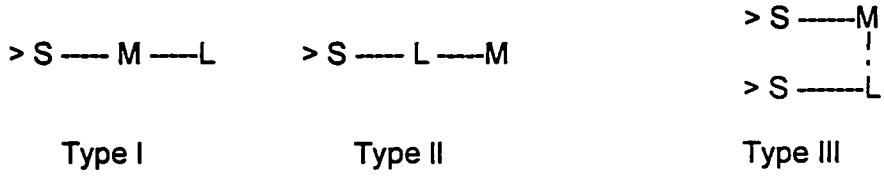


Fig. 1 Proposed surface complexes formed by adsorbed picolinate and 2,3-PDCA ions. From Davis and Leckie (1978)

When the presence of organic ligands enhances metal ion adsorption to the solid phase, it is likely that ternary complexes have formed. Three types of ternary complexes are possible (Davis and Leckie, 1979):



Type I Type II Type III

where S represents a surface adsorption site, L denotes a complexing ligand, and M is a metal ion. For example, complexes of type II or III are plausible in the presence of 2,3-PDCA in Davis and Leckie's study (Davis and Leckie, 1978). With regard to configuration I, Stadler and Schindler (1994) observed enhanced uptake of Cu^{2+} on Ca-montmorillonite in the presence of malonate and proposed the existence of ternary surface complexes of type I. However, it should be pointed out that natural DOC consists of various compounds with different configurations of functional groups, and ternary complex formation in soil and aquifer systems may be much more complicated than the mechanisms suggested by model ligands and well-defined surfaces.

At the present time, the role of DOC in promoting or inhibiting metal ion adsorption is still ambiguous. The formation of ternary complexes can promote metal adsorption on the solid phase, but this increased adsorption can be compensated by other forms of interactions. Dissolved ligands may compete with the solid phase for the metal cation, causing decreased adsorption of the metal. In order to model the transport of heavy metals in soil and other aquatic system, additional experimental work is needed in the future.

PART I. DISSOLVED ORGANIC CARBON IN A SLUDGE-AMENDED SOIL

INTRODUCTION

At present , land application of municipal sewage sludge and other biosolids is considered an important means for disposal and recycling of the wastes. However, these biosolids may contain potentially harmful substances like heavy metals, various organic compounds, pathogenic agents, etc. (Holtzclaw and Sposito, 1978; Alloway, 1990). Among these substances, heavy metals are considered of primary concern since their non-biodegradability can result in accumulation in the soil from which they may be transferred to aquifers, crops, and animals (Sidle et al., 1976; Chang et al., 1984). The mobilization and transport of heavy metals in soil is controlled by many factors, including pH, Eh, mineralogy, and interactions of the metal ions with inorganic anions and organic ligands. Organic ligands, particularly dissolved ones, are especially reactive with heavy metals due to complexation reactions and may play a significant role in determining the mobility of these metals in soil environment.

Sewage sludge is very rich in various organic compounds, including aliphatic and aromatic acids, polysaccharides, proteinaceous material, humic substances and organic sulfonates, etc. (Holtzclaw and Sposito, 1978; Holtzclaw et al., 1980; Boyd et al., 1980; and Baham and Sposito, 1983). Its application to soil is expected to affect the content and composition of soil DOC, which, in turn, would influence the speciation, mobility and fate of the heavy metals in the amended soils. The objective of this study was to determine the changes in DOC content and composition in a soil due to sludge amendment. The DOC extracted from the soil was fractionated and characterized according to molecular sizes and XAD-8 resin chromatography.

MATERIALS AND METHODS

Soil samples

Soil samples were collected from a sludge-amended experimental field near the City of Ames Water Pollution Control Facility (WPCF), Ames, IA.. The soil is a fine-loamy, mixed, mesic Cumulic Haplaquoll (Thompson and Scharf, 1994). The field was under two vegetation treatments: switchgrass (*Panicum Virgatum*) and trees of poplar-cottonwood hybrid (*populus* x *euramericaner*-clone NC-5326). Over a 2-year period, this field had received secondarily treated sewage sludge amendments at the cumulative rates of approximately 0, 22, and 42 Mg dry sludge ha^{-1}. Sewage sludge (about 5 % solids) was applied by spraying onto the soil surface from a large application truck. The samples were taken in April 1993, approximately one month after the most recent sludge amendment. Samples were collected from the middle portions of 15 x 60 m plots, where sludge application was most uniform. Surface (0-5 cm) and subsurface (5-25 cm) soil samples were collected at single location int two replicate plots of each treatment by using a 2.5 cm-diameter hard proble. The samples were stored at field moisture content at ~ $4^{o}C$ and passed through a 2-mm sieve just before use.

Extraction of dissolved organic carbon

Dissolved organic C from field-moist soil samples was extracted with 0.1 mM $CaCl_2$ (dry soil:water, 1:10). The 0.1 mM $CaCl_2$ solution has a low ionic strength typical of precipitation in Iowa (NADP, 1994). The soil / $CaCl_2$ solution suspensions were shaken overnight on a mechanical shaker and then centrifuged at 1,500 rpm for 10 min (radius 19 cm) The supernatants were subsequently centrifuged at 7,600 rpm for 10 min by using a small fixed angle centrifuge (radius 10 cm). According to Jackson's equation (1975) for particle setting time under centrifugal acceleration, only materials with effective particle

radii less than 0.02 μm (assumed to have a particle density of 1.5 g cm^{-3}) remained in the final, collected solutions. For sequential extraction, the procedure given above was repeated several times on the same soil sample. The extracted DOC solutions collected were reduced 2- to 8- fold by vacuum-rotary evaporation at 40 ^{o}C. The concentrated solutions were adjusted to pH 4 , stored at 4 ^{o}C, and used as soon as possible for DOC fractionation within 24 hr.

Molecular-weight fractionation

The molecular-weight (MW) fractionation was accomplished by dialysis of concentrated DOC solutions at a nominal molecular-weight cutoff of 12,000-14,000 daltons (hereafter referred to as 14,000 daltons). The concentrations of DOC in soil extracts were too low to yield meaningful results with more fractions with the dialysis technique (Homann and Grigal, 1992). DOC solutions were dialyzed against distilled and deionized water external to the dialysis membranes maintained at pH 4 and ~ 4 ^{o}C to minimize microbial activity. The ratio of DOC solution to diazylate was 1:10 for most of the soil samples. Diazylate was stirred often and changed daily for 3 days. The diazylates of each fraction were combined, concentrated by rotary evaporation as before to about 200 ml, and adjusted to pH 2 for further fractionation. Final, dialyzed DOC solutions (MW > 14,000 fraction) were adjusted to pH 2, and centrifuged at 7,600 rpm for 10 min to separate acid-soluble organics such as fulvic acids from acid-insoluble organics such as humic acids. The acid-insoluble organic fraction with MW > 14,000 was referred to as "colloidal" organic C. it is likely that those humic substances were intimately associated with inorganic colloidal material as well.

Hydrophilic / hydrophobic fractionation

The fractionation procedures of Leenheer and Huffman (1979) were used with some simplifications. Adsorption chromatography using an XAD-8 resin (Supelco, Bellefonte, PA) was utilized to fractionate the DOC present in each weight fraction (except the colloidal organic fraction) into hydrophilic and hydrophobic fractions. First, the resin cleanup procedure of Thurman and Malcolm (1981) was performed to remove organic and inorganic impurities from the XAD resin. The size of XAD-8 column was chosen according to Leenheer's (1981) equation:

$$V_{EL} = 2\ V_0\ (1+k')$$

V_{EL} is the volume of sample that is applied to the column;

V_0 is the void volume of the column (~ 65 % of the bed volume);

k' is the column capacity factor (defined as 50).

The sizes of columns used varied between 2 and 3 ml.

The DOC solution at pH 2 was pumped through a resin column at a flow rate of 15 bed volume / h. Effluent from the column was collected and designated as the hydrophilic subcomponent. The column was backflushed with 0.1M NaOH, the eluent representing the hydrophobic acids. The organic fraction which was adsorbed as the XAD-8 column and not desorbed by 0.1N NaOH was defined as hydrophobic neutrals and quantified by the difference between total input DOC and DOC of the hydrophilic fraction plus DOC of the hydrophobic acids. Preliminary analyses indicated that hydrophobic bases, which were adsorbed on XAD-8 at pH 7 and desorbed by dilute HCl, were insignificant in both sludge and soil samples and were included in the hydrophilic fraction.

Chemical analyses

Major soil physical and chemical properties are reported in Table 1-1, and more detailed information may be found in ISTART (1996). The particle size distribution of the

Table 1-1. The major soil chemical and physical characteristics

Depth (cm)	pH	Particle Size Distribution (g / kg^{-1}) sand	silt	clay	CEC (cmol kg^{-1})	Free Fe and Mn oxides (g kg^{-1})
0 - 28	6.1	250	370	380	28.2	6.63

aquifer material was determined by the pipette technique (Walter et al., 1978). Cation exchange capacity was determined byexchange with ammonium acetate and pH 7 (Thomas, 1982). The Fe and Mn contents were measured by CBD extraction of Franzmeier et al. (1977). The pH of the aquifer material was measured at the ratio of 1:1 of solid to water, and total carbon was determined by high-temperature combustion (Nelson and Sommers, 1982). DOC determinations were performed using a TOC-5050 (Shimadzu) carbon analyzer with an IR detector. All DOC analyses were conducted on samples from each of the two replicate plots. The data determined were presented in Appendex I, and the average values of the two replications are reported in the text.

RESULTS AND DISCUSSION

Changes of total soil organic matter content

The digested municipal sludge applied to the field plots had a typical total organic C content of ~ 300 g C kg^{-1} dry weight. Although a fraction of the organic carbon in the material is expected to be readily decomposible when added to an aerobic soil, the major portion of organic substances is resistant to decomposition (Agbim et al., 1977; Sommers et al., 1976; and Terry et al., 1979). The residual sludge C can be incorporated into soil humic substances and accumulate in soils (Terry et al., 1979; Varanka et al., 1976).

Considerable accumulation of organic C in the soil, particularly in the surface layer, was observed in the field plots at high sludge application rates (Table 1-2). Because the sludge was applied by surface spraying, the increase of organic carbon in the deeper soil layers is probably due to the increase in root residues induced by sludge application. Downward movement of a mobile organic phase from the soil surface may also be responsible for the increase in soil organic C in the deeper soil.

Table 1-2. The changes of soil organic carbon contents after two years of sludge application (1991-1993)

Treatment	0 dry Mg ha^{-1}	22 dry Mg ha^{-1}	42 dry Mg ha^{-1}
Depth	.....	g kg^{-1} soil	.....
		Switchgrass	
0 - 5 cm	27.2	33.2	48.6
5 - 25 cm	24.1	26.7	29.3
		Hybrid Poplar	
0 - 5 cm	29.8	31.4	34.9
5 - 25 cm	26.4	26.7	29.8

Soil dissolved organic carbon under different treatments

Levels of extractable dissolved organic carbon. Data presented in Fig. 1-1 show that extractable DOC levels of both switchgrass- and poplar-vegetated soils were increased by sludge applications. The application of 42 Mg / ha of digested sludge resulted in DOC contents of surface samples two- to three-fold greater than samples of untreated soil. The DOC level at 5-25 cm depth at an application rate of 42 Mg / ha also significantly increased compared to untreated subsurface soil. The significant increase in DOC contents in sludge-amended plots may be attributed to the changes induced by sludge application, for example:

1) direct introduction of soluble organic C into soil
2) increase in plant residues by stimulating the growth of switchgrass and poplar
3) possible increase in numbers of soil microorganisms and activities of many enzymes (Varanka et al., 1976), enhancing the transformation of insoluble organic carbon into soluble organic C.

The increase in DOC levels due to sludge application was observed to be greater under switchgrass than under poplar (Fig. 1-1). The role of the vegetation cover in increasing in DOC levels may be related to the amount of the plant residues, their mode of addition into the soil and the nature of their decomposition. It is widely known that sludge facilitates rapid establishment and vigorous growth of grass. Sludge-amended sites generally have a greater areal cover of vegetation and greater yield of biomass (Sopper, 1993). The better the growth of the grass, the more the root systems are developed. So a large amount of fine root residues, being raw material for DOC production, accumulate in the soil under perennial switchgrass. Compared with switchgrass, the roots of woody poplar are mainly coarse, thick and long-living, adding only small amounts of root residues

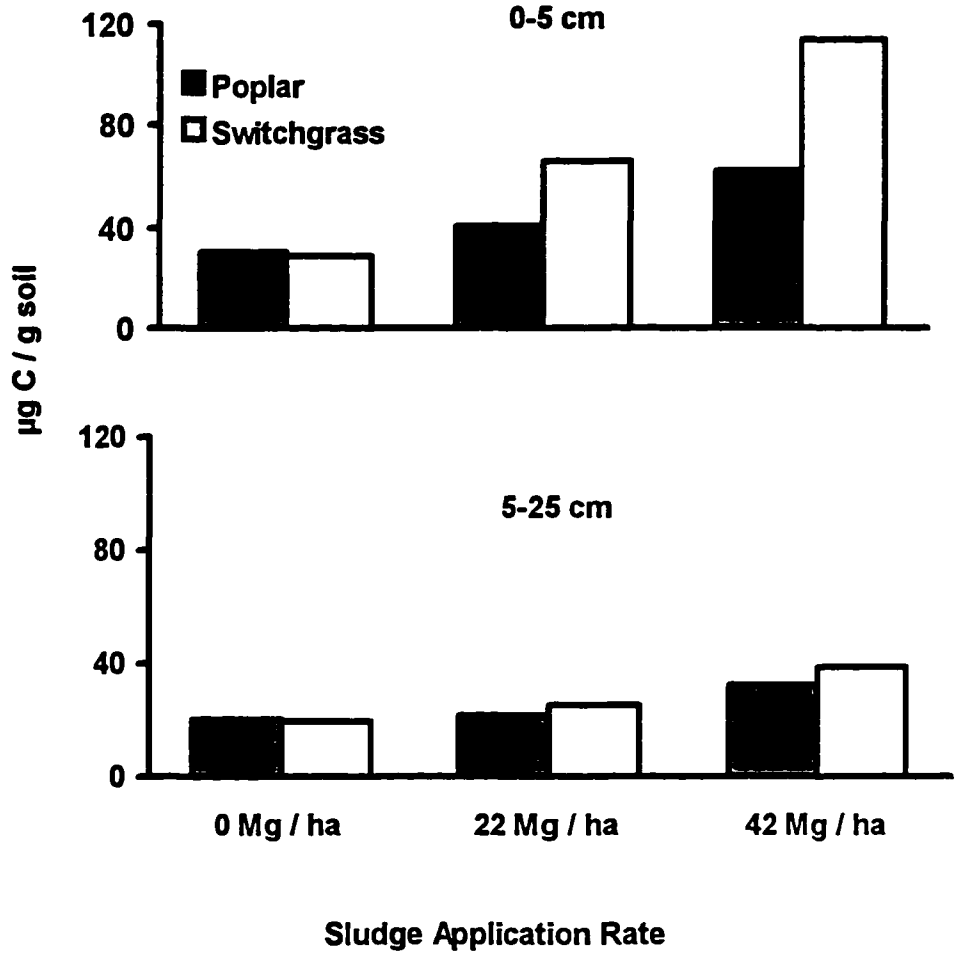


Fig. 1-1 Extractable DOC levels in the sludge-amended soil

into the soil. The leaf litter, the main source of organic matter under trees, concentrates only in the litter layer at the soil surface; and organic matter enters the soil layers in the form of solution leached from the litter. Thus, a higher level of soil DOC is expected under switchgrass than under poplar.

Generally, it is believed that soluble organic C can be easily utilized by microbes in cultivated soil. Our findings suggest that, under permanent grass, a significant portion of soluble organic C may actually accumulate in a sludge-amended soil, with potential to influence metal speciation and mobility in the soil.

Molecular weight fractionation. Extractable DOC from zero-sludge plots contained approximately equal percentages of the fraction with MW < 14,000 daltons and the fraction with MW > 14,000 daltons under either switchgrass or poplar tree (Fig. 1-2 and Fig. 1-3). However, sludge application shifted the MW distribution to lower values, although both the concentrations of high molecular-weight and low molecular-weight DOC increased. This trend was more pronounced under the switchgrass (Fig. 1-2). The significance of the increase in smaller organic C compounds in terms of influencing metal transport in the sludge-amended soil needs to be further investigated.

Hydrophilic / hydrophobic characteristics. As the rate of sludge application increased, both hydrophilic and hydrophobic fractions of extractable DOC were markedly increased (Fig. 1-4 and Fig. 1-5). Under switchgrass, the observed increase was greater for the hydrophilic than the hydrophobic subcomponents in the surface zone (0-5 cm). However, the level of the hydrophilic subcomponent was significantly higher than the corresponding hydrophobic subcomponent in all the plots, regardless of treatments. It has been reported that hydrophilic components of DOC are more mobile than hydrophobic components in porous media (Dunnivant et al., 1992a). And hydrophilic components

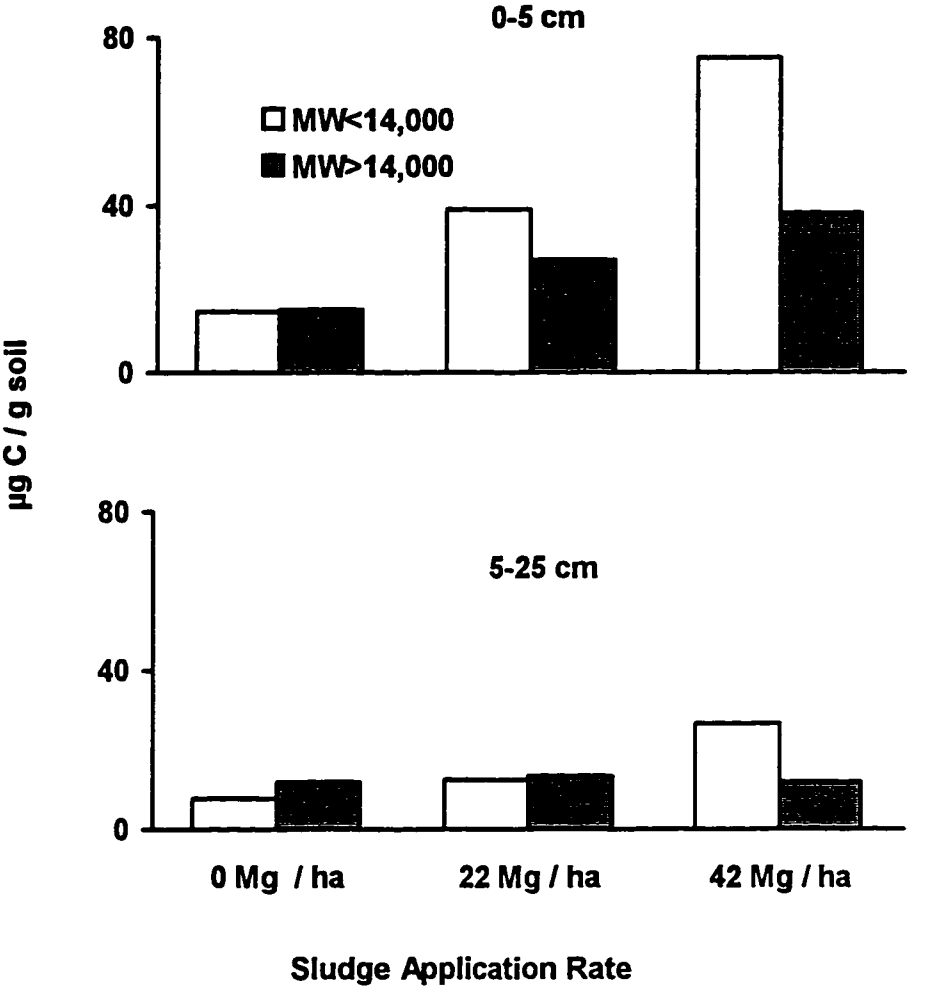


Fig. 1-2 Molecular weight fractionation of DOC in the sludge-amended soil under switchgrass

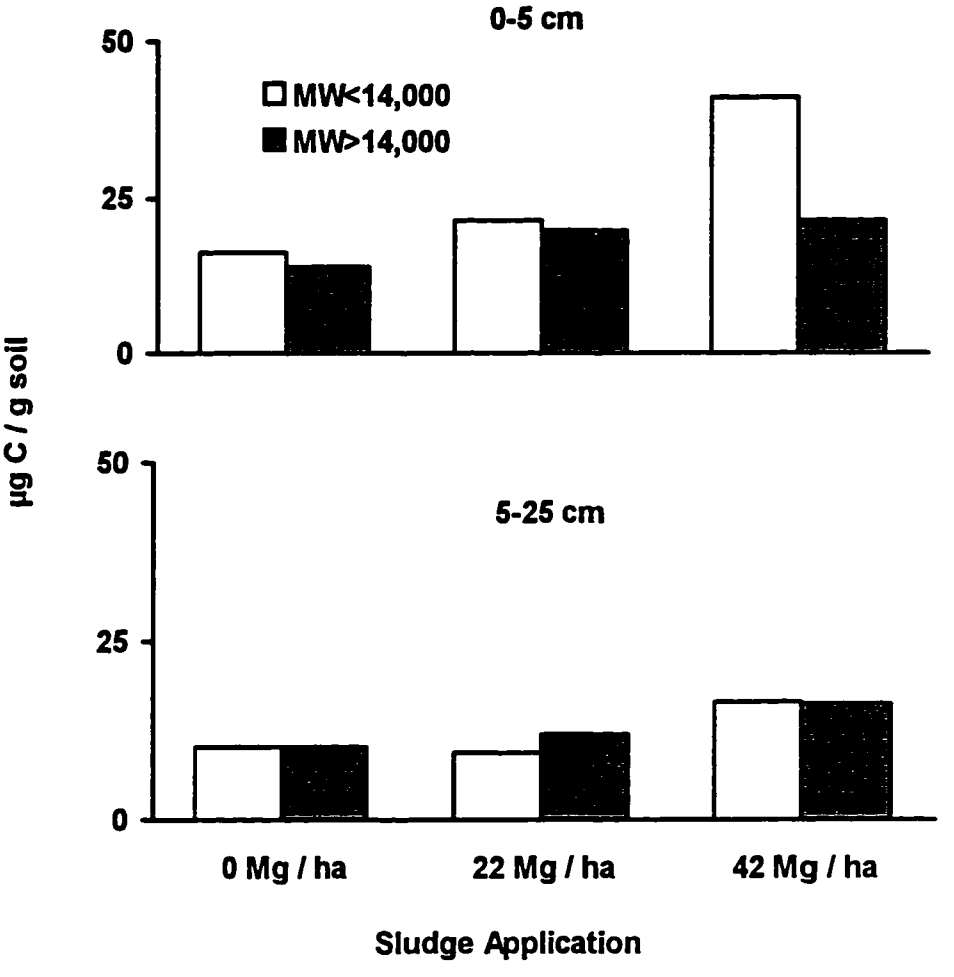


Fig. 1-3 Molecular weight fractionation of DOC in the sludge-amended soil under poplar

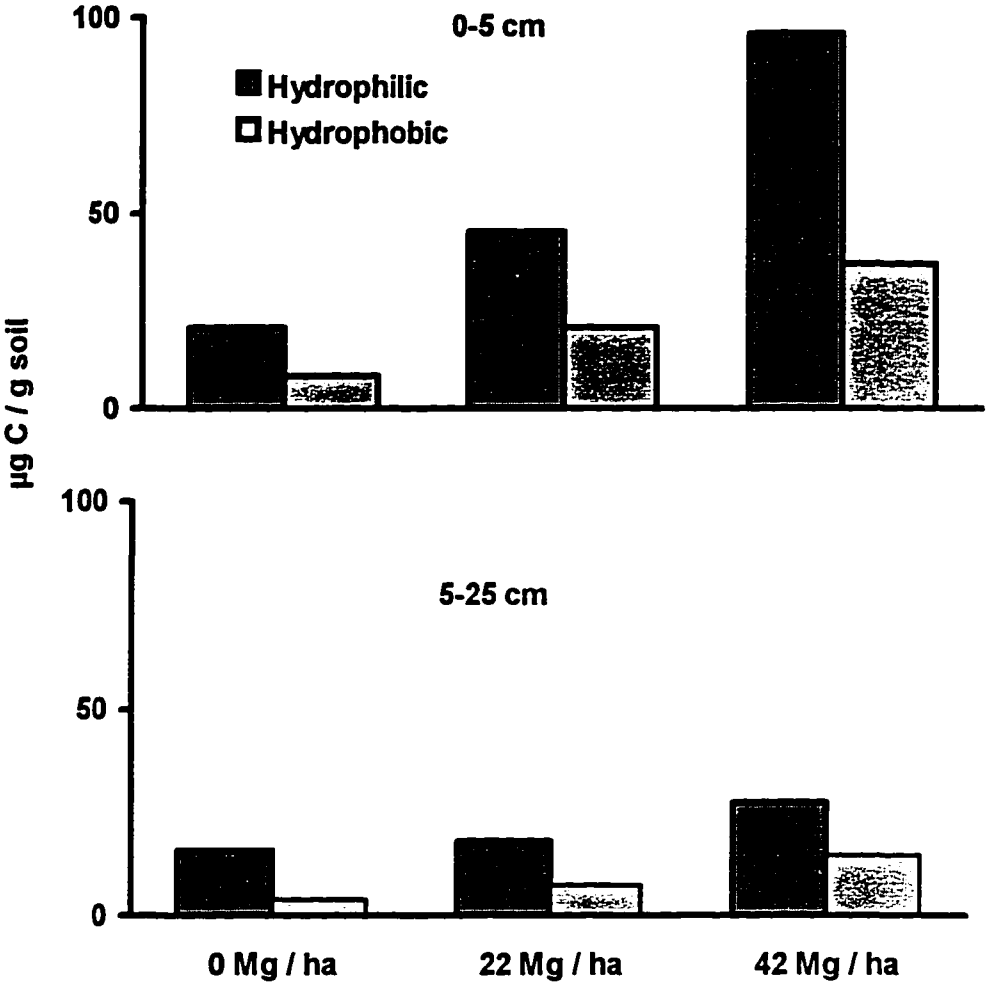


Fig. 1-4 Hydrophilic / hydrophobic characteristics of soil DOC under switchgrass

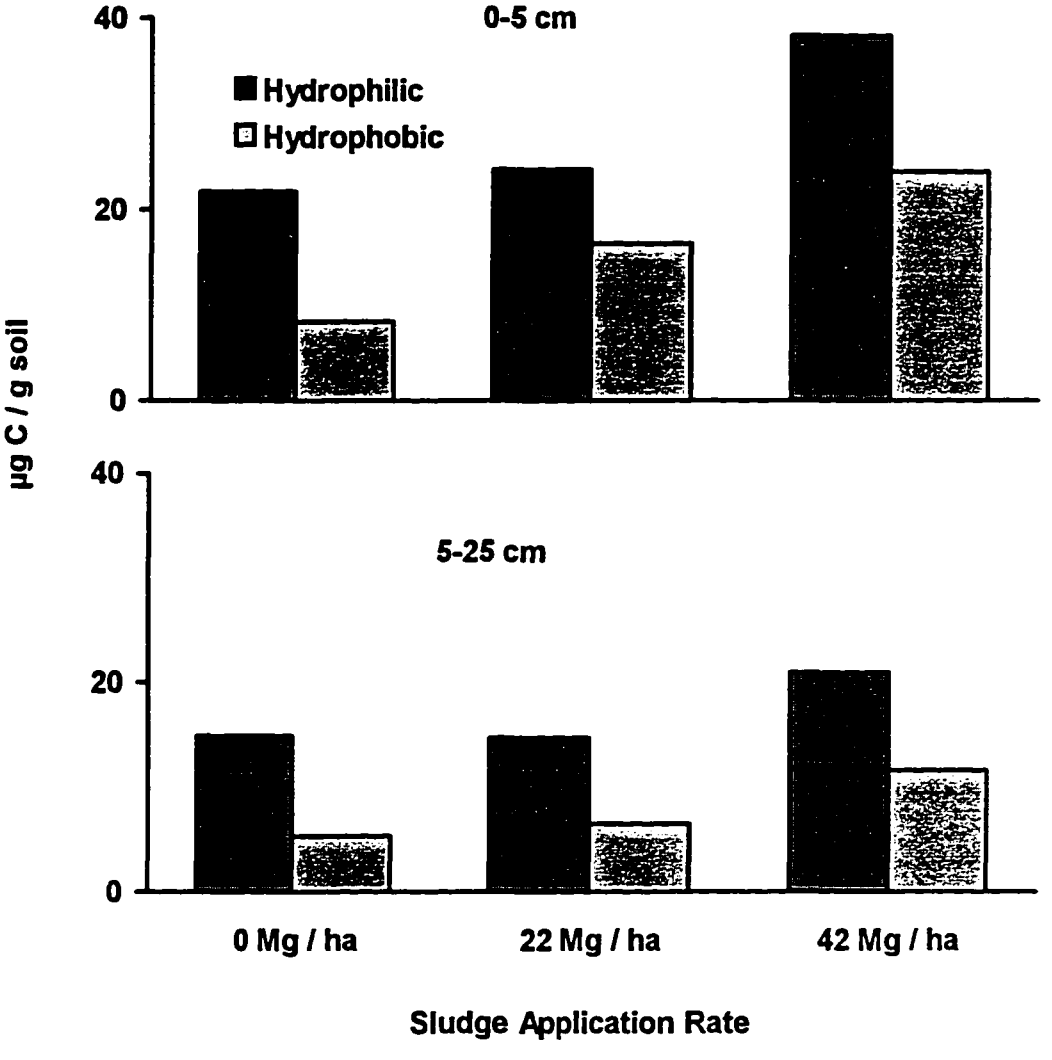


Fig. 1-5 Hydrophilic / hydrophobic characteristics of soil DOC under poplar

contain high concentrations of hydroxyl and carboxyl functional groups for metal complexation (Leenheer, 1981). Thus, the higher levels of hydrophilic fractions suggest that this DOC fraction may have a greater impact on metal movement in the sludge-amended soil (Dunnivant et al., 1992a). However, this hypothesis needs to be further tested.

Distribution of hydrophilic / hydrophobic subcomponents in different weight fractions. The distributions of hydrophilic and hydrophobic subcomponents in each weight fraction under switchgrass are presented in Fig. 1-6 - Fig. 1-8. Similar distributions were also observed under poplar. Under switchgrass, the distribution of hydrophilic components was approximately equal in the fraction with MW < 14,000 and the fraction with MW > 14,000 for the surface zones (0-5 cm) of zero-sludge plots (Fig. 1-6). For the subsurface zones (5-25 cm) of the same plots, hydrophilic components were slightly richer in the fraction with MW > 14,000. However, at the application rate of 42 t / ha, hydrophilic components became more abundant in the fraction with MW < 14,000. In other words, the sludge application increased the level of hydrophilic components with low MW in the soil. Hydrophobic acids and neutrals of soil DOC were also observed to be concentrated in the fraction with MW < 14,000 at the application rate of 42 t / ha (Fig. 1-7 and Fig.1-8). The hydrophobic subcomponents defined in this study are similar to traditionally defined fulvic acids (adsorbed by XAD-8 resin at pH 2) (Stevenson, 1982). Sposito et al. (1982) observed that fulvic acids extracted from sludge-amended soils very much resembled typical sludge-derived fulvic acids in terms of chemical composition and functional groups. In this study, it is also likely that the major portion of the hydrophobic subcomponents of soil DOC, as well as hydrophilic subcomponents, originated directly from the sludge.

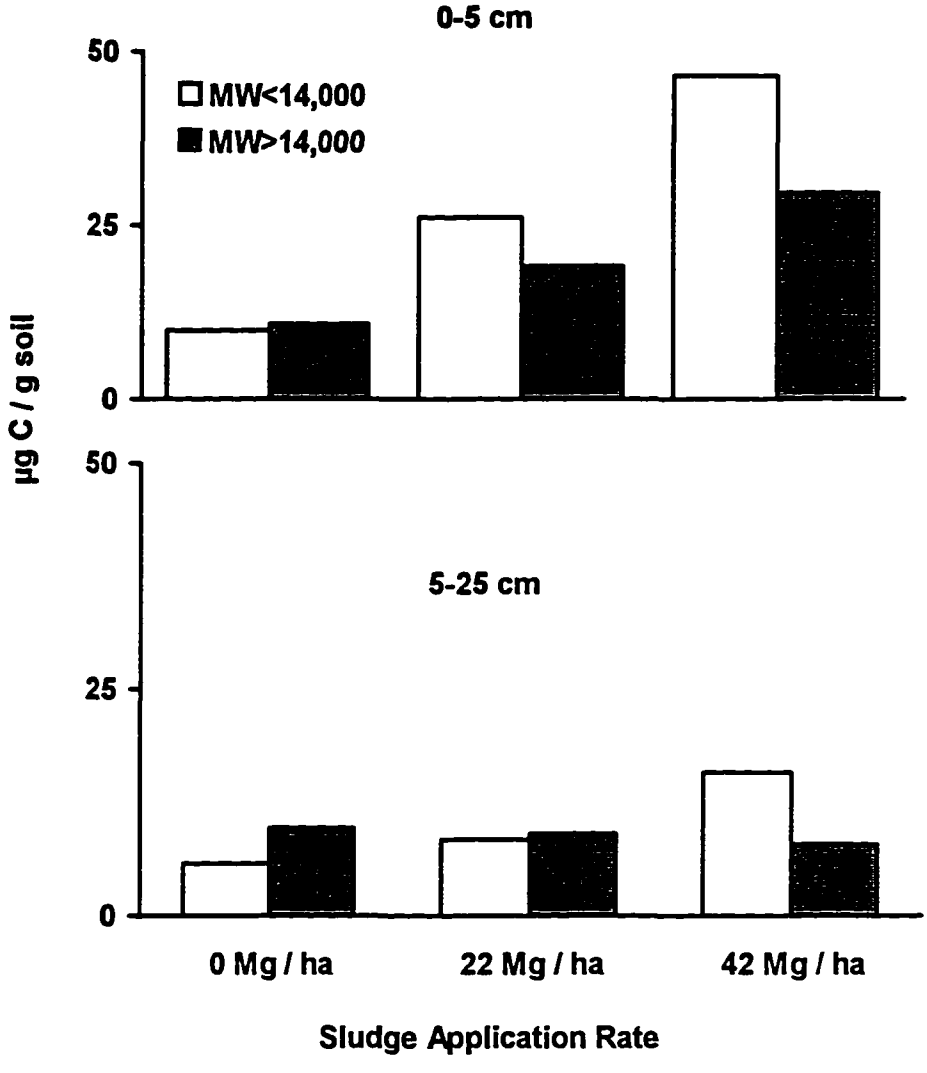


Fig. 1-6 Hydrophilic DOC in different weight fractions under switchgrass

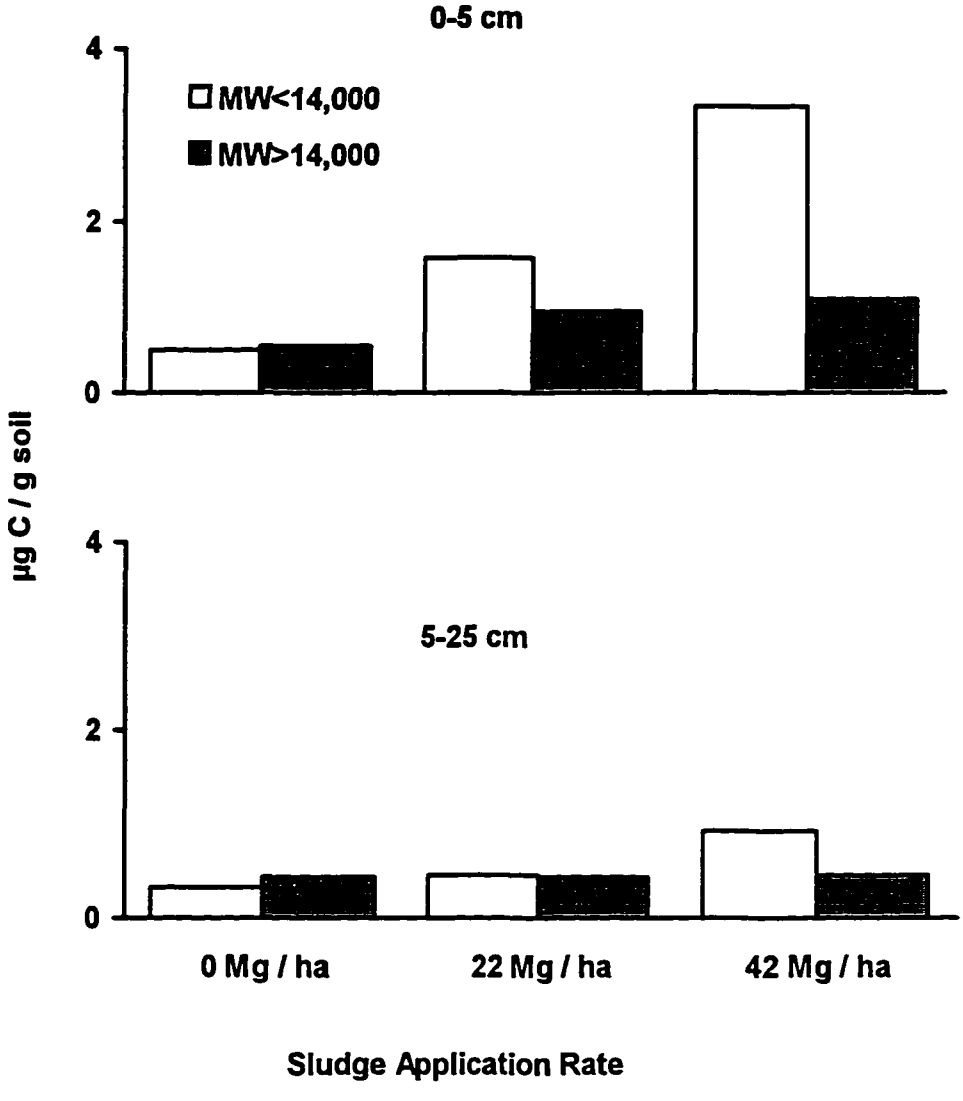


Fig. 1-7 Hydrophobic acids in different weight fractions under switchgrass

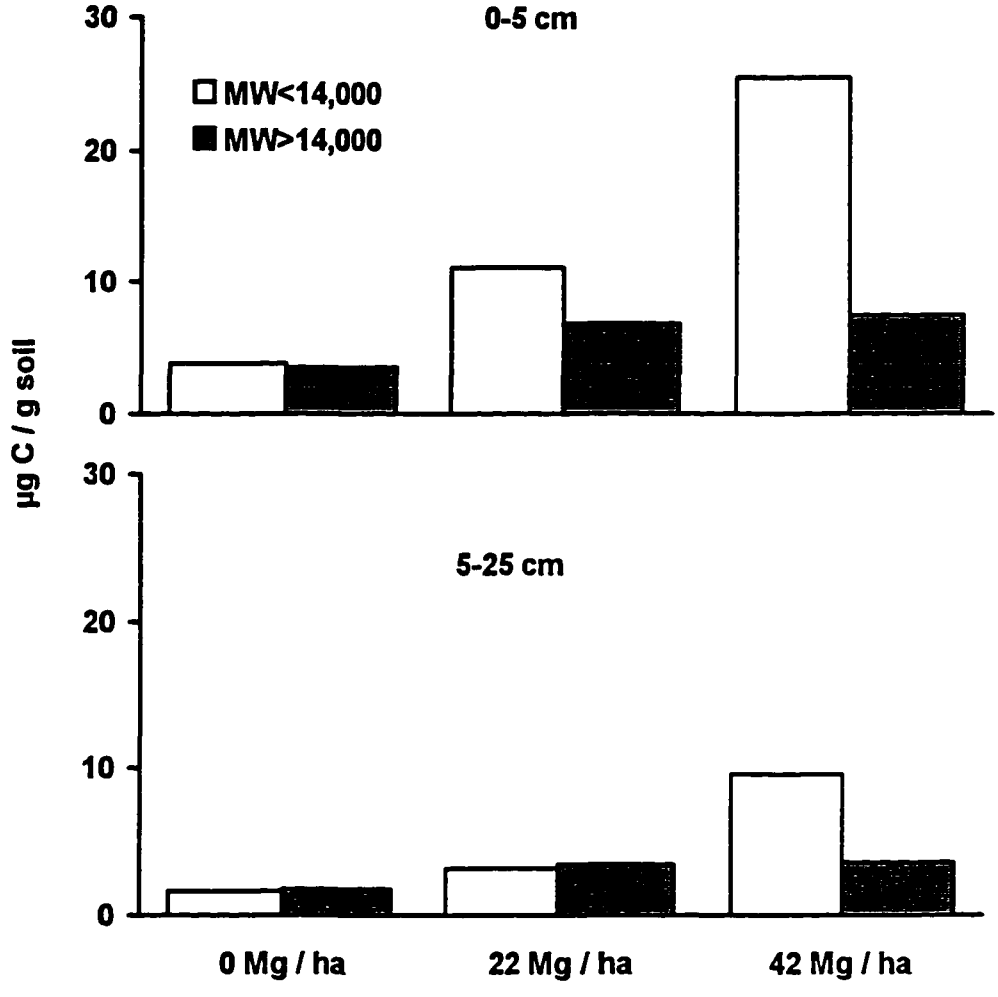


Fig. 1-8 Hydrophobic neutrals in different weight fractions under switchgrass

"Colloidal" organic carbon

Colloidal organic material in natural waters has recently been an active research area because of its potential importance in the transport of heavy metals and organic contaminants (McCarthy and Zachara, 1989). The organic colloid fraction, as defined by our technique (precipitated at pH 2), is presumably dominated by humic acids. Fig. 1-9 reveals that the surface zones (0-5 cm) yielded much less extractable organic colloidal material as the rate of sludge addition increased. The electrical conductivity data of soil extracts (given in Fig. 1-10) and sludge suspension indicated that large amounts of salts were introduced into the soil through sludge application, causing colloidal materials to be coagulated.

Since only small amounts of colloidal organic C can be extracted from the soil with a high rate of sludge application, are colloidal organics possibly mobile in the sludge-amended soil? To address this question, sequential extraction of DOC and suspendable organic C was performed on one sample from the 42 Mg / ha treatment and one sample from the 22 Mg / ha treatment. Extractions were repeated until the same ionic strength as in the extract from the zero-sludge plot was reached. Fig. 1-10 and Fig. 1-11 show that the concentration of DOC in extracts decreased and colloidal organic C increased with increase in the numbers of extraction. These results suggest that DOC may be readily mobilized from the sludge-amended soil, but that colloidal organic C would become mobile only after the salts are leached.

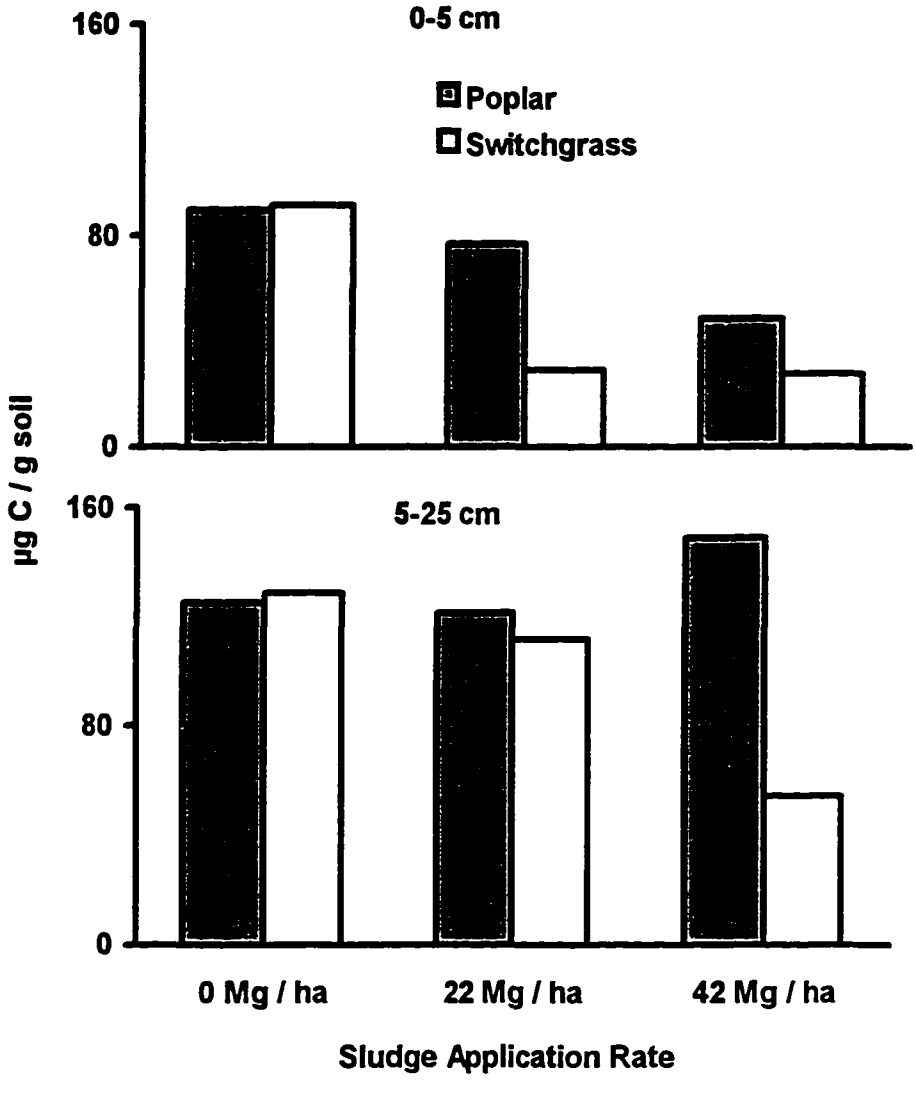


Fig. 1-9 Colloidal organic C in the sludge- amended soil

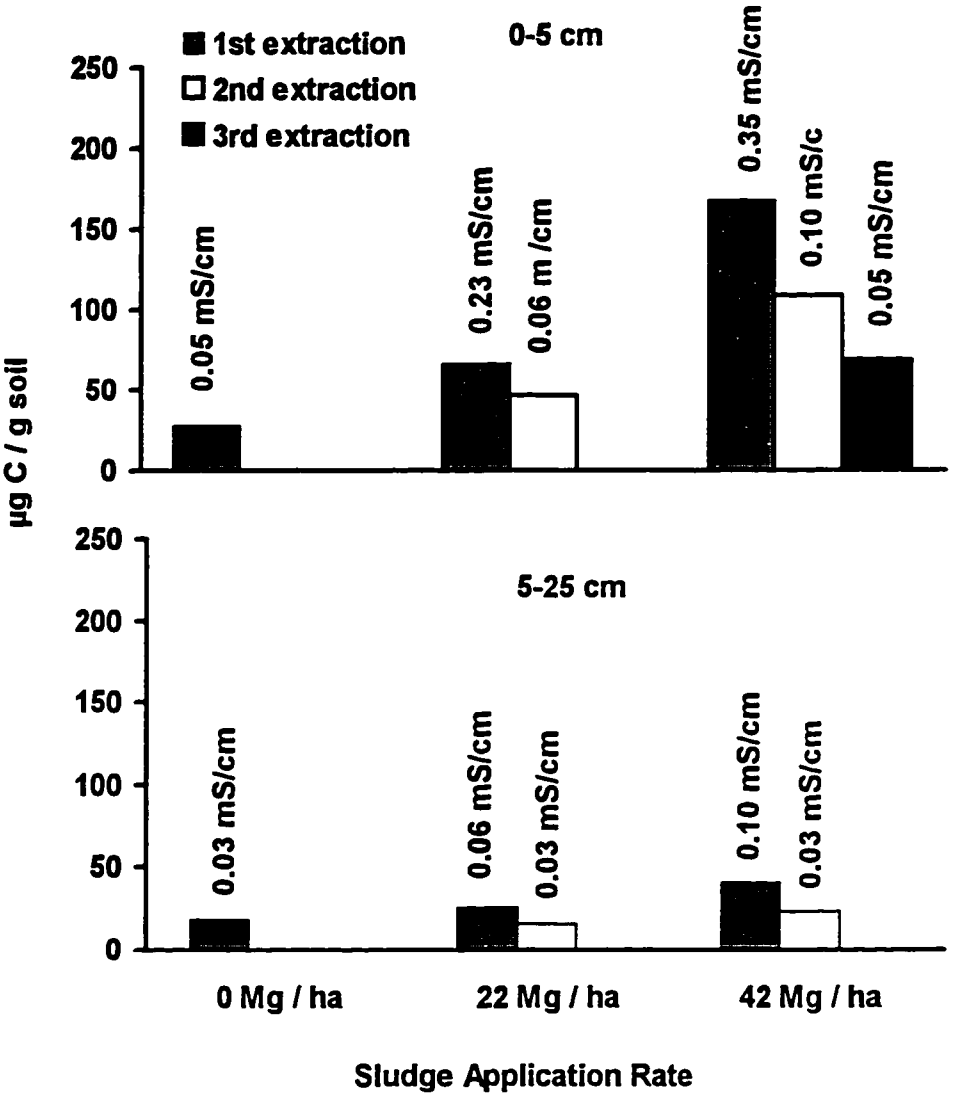


Fig. 1 - 10 Changes of DOC with sequential extraction under switchgrass

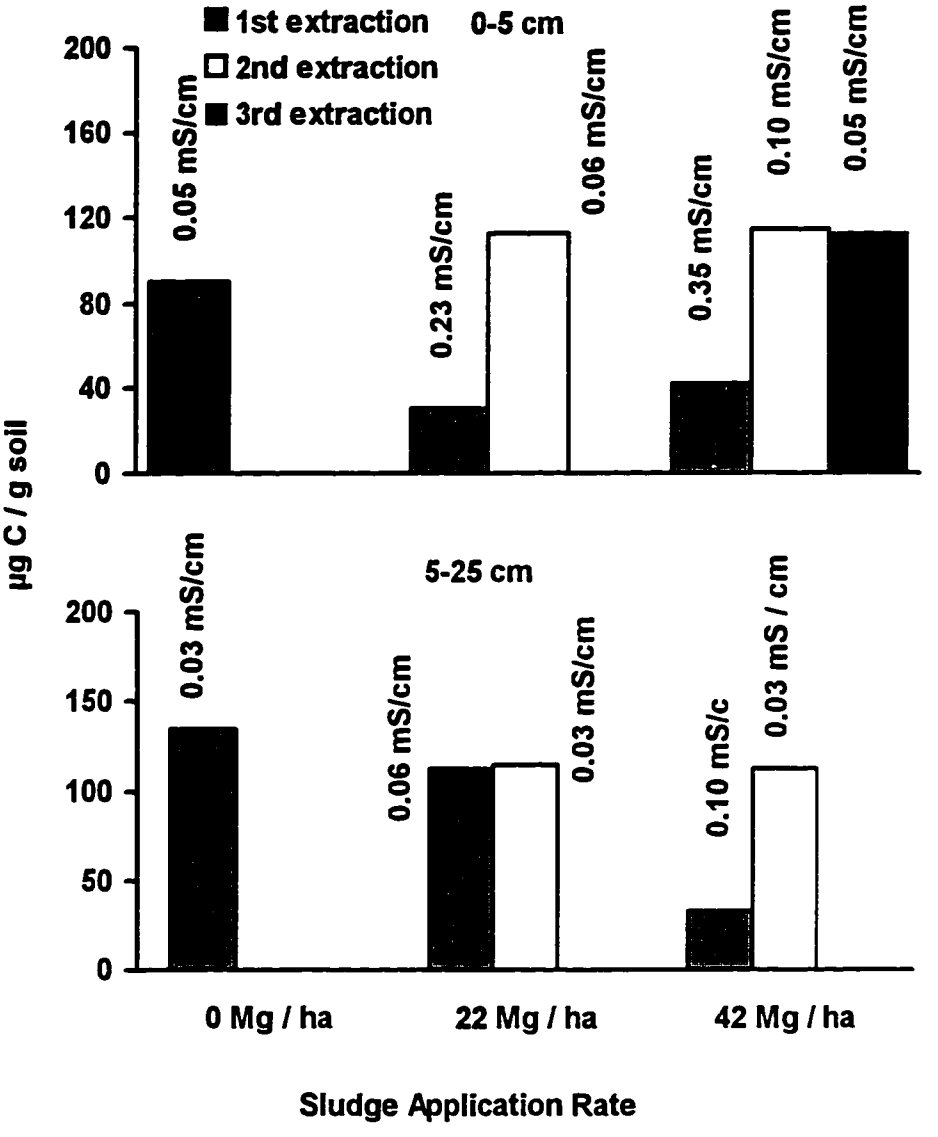


Fig. 1 - 11 Changes of "colloidal" organic C with sequential extraction under switchgrass

CONCLUSIONS

An investigation was performed to characterize the soluble and suspendable organic matter in a sludge-amended Cumulic Haplaqudoll under two vegetation treatments: switchgrass and hybrid poplar. The soil organic C that could be dispersed in 0.1 mM $CaCl_2$ was fractionated according to molecular weight and XAD-8 resin chromatography. Under both types of vegetation, addition of sludge greatly increased the amount of soluble organic C in the soil, particularly under switchgrass. Sludge application shifted the MW distribution of extractable DOC in soil to lower weights (<14,000 daltons). The concentrations of hydrophilic DOC subcomponents were found to significantly exceed those of hydrophobic DOC in all treatments, although sludge application increased the levels of both hydrophilic and hydrophobic subcomponents. As the rate of sludge addition increased, the surface zones (0-5 cm) yielded smaller amounts of extractable "colloidal" organics (dominated by humic substances) due to high salt levels induced by sludge application. Sequential extractions suggested that large amounts of the "colloidal" organics could be mobilized from the soil only by removal of the salts.

PART II. COPPER (II)-BINDING ABILITY OF DOC DERIVED FROM ANAEROBICALLY DIGESTED SEWAGE SLUDGE

INTRODUCTION

The mobility and bioavailability of potentially hazardous heavy metals in agricultural soils amended with sewage sludge are closely related to the interactions of the metal ions with soluble soil organic ligands or sludge-derived organic ligands. Thus studies of the chemical and metal-binding properties in sludge or sludge-amended soils have flourished for last three decades, and most of these studies have tried to identify the individual compounds and metal-binding sites (e.g. Sposito and Holtzclaw, 1977; Cothern et al., 1977; Boyd et al., 1979, Holtzclaw et al. 1980; Baham and Sposito, 1983; Dudley et al., 1987). But the dissolved organic ligands derived from soil or sludge are extremely heterogeneous, and they contain a myriad of compounds with various functional groups. Technically, it is difficult to isolate and positively identify more than a small fraction of the compounds or functional groups. However, separation of dissolved organic compounds (DOC) into broad subcomponents with similar properties and characterization of the metal binding capacity of these subcomponents would easily offer valuable information on metal-ligand complexation properties.

Leenheer and Huffman (1979) and Leenheer (1981) developed a fractionation and isolation approach that separates DOC into hydrophobic and hydrophilic subcomponents by XAD-8 resin chromatography. This approach has been used for a further characterization of metal-binding properties of different subcomponents (Guggenberger et al., 1994). Guggenberger et al. (1994) reported that the Cr- and Cu-binding by hydrophilic acids collected from water percolated through a Spodosol exceeded that of hydrophobic acids by 2-8 times. Molecular weight distributions of DOC should also be correlated with metal-binding behavior, but investigations of the metal-binding capacity of DOC with different molecular weights are relatively scarce. In one study, Kuiters and Mulder (1992)

observed that apparently low-MW DOC was responsible for 50 - 99 % of the Cu-binding in the litter extracts of birch, beech, fir, oak, pine and poplar.

Metal-binding capacities of various organics have been studied by different techniques in the past, including metal-ion retention by cation-exchange resin (Crosser and Allen, 1977), dialysis (Zunino and Martin, 1977), ion-selective electrodes (Fitch et al., 1986) and gel permeation chromatography (Kuiters and Mulder, 1992). Of these techniques, the ion-selective electrode (ISE) is a very popular technique (Bhat et al., 1981). The metal-binding ability of DOC in an aqueous solution is measured by adding excess metal ion to the solution and distinguishing free metal ions and complexed metal ion concentration by an ion-selective electrode. Fitch et al. (1986) reported that a Cu-ISE permits measurement to be made at low concentrations of the metal ion (pCu 8). This is important to natural systems where Cu concentration in aqueous phase and percentage saturation of Cu in organic material are expected to be low.

The purpose of this study was to characterize and isolate DOC derived from an anaerobically digested sewage sludge into broad subcomponents by using a combination of molecular weight fractionation and XAD-8 resin chromatography. The metal-binding abilities of the isolated subcomponents were then evaluated by the ISE technique. Copper was chosen as the model metal ion because of its high affinity for most of organic ligands and its high abundance in many sludge materials (Alloway, 1990; McBride, 1994).

MATERIALS AND METHODS

Preparation of DOC solution

Anaerobically digested sewage sludge was sampled in liquid form from the Water Pollution Control Facility at Ames, IA. The solid content in the liquid sludge was 5%. The sludge suspension was centrifuged at 1500 rpm for 10 min to remove large solid particles. The DOC solution was obtained by further centrifuging the supernatant at 7600 rpm for 10 min and collecting the second supernatant.

DOC solution collected from the liquid sludge sample was reduced in volume ~ 2.5 fold by vacuum-rotary evaporation at 40 °C. The concentrated solution was adjusted to pH 2 and centrifuged at 7600 rpm for 5 min to separate acid-soluble organics from acid-insoluble organics, mainly humic acids. Acid-insoluble compounds were removed from the DOC solution simply because these materials would clog pores in the resin columns during further DOC fractionation.

Fractionation of DOC into more subcomponents

Molecular-weight fractionation. During the isolation of sludge DOC, a significant amount of salt was also extracted. The salts could be various inorganic complexing ligands such as SO_4^{2-} and Cl^- or inorganic cations like Ca^{2+}. Unfortunately, the presence of salts complicates the speciation in solution phase for the determination of Cu-binding ability. Thus, the nominal MW cutoffs of DOC were 500, 3500 and 14,000 daltons, with MW < 500-dalton fraction excluded from the study, since salts were concentrated in this fraction. The DOC solution was dialyzed against distilled and deionized water external to the dialysis membranes (MW cutoff at 14,000 daltons) at pH 4 and ~4 °C to minimize

microbial activities. The ratio of DOC solution to dialyzate was 1:20 and dialyzate was changed daily until free DOC was reached. The dialyzates were combined, concentrated by rotary-vacuum evaporation and continually dialyzed with lower MW-cutoff membranes.

Hydrophilic / hydrophobic fractionation. Each molecular-weight fraction was further fractionated by XAD-8 resin chromatography. The DOC solutions were operationally defined as the total hydrophilic (Hi, passing through the resin column), hydrophobic acid (Hb, being adsorbed by the resin column and desorbed by 0.1 M NaOH), and hydrophobic neutral (Hn, being adsorbed by the column and not desorbed by the base) subcomponents. The hydrophobic neutrals were isolated by Soxhlet extraction of the resin with methanol and subsequent evaporation of excess methanol. The Na^+ and Cl^- introduced into the solution during desorbing Hb and pH adjustment were removed by further dialysis. The detailed procedure was described in Part I.

Cu-binding ability of DOC subcomponents

Apparatus. An Orion model 94-29 Cu^{2+}-ISE, a reference electrode Orion model 900200, and a Corning model 135 pH / ion meter were used for determination of Cu-binding ability. The crystal membrane of Cu electrode was polished with a polishing strip and equilibrated in 7.87×10^{-4} mole Cu / L Cu solution for at least 30 min before use.

Procedure. Aliquots of 30 ml of 0.1 M KNO_3 solutions containing free Cu^{2+} ranging from 1.57×10^{-6} to 3.94×10^{-5} M were added to a set of beakers and adjusted slowly to pH 6 with a dilute solution of KOH in 0.1 M KNO_3. The concentrations of Cu^{2+} were measured with the Cu-ISE and a calibration curve was therefore obtained. Aliquots of 10 ml of 4.17×10^{-3} mole C DOC solutions were added to the solutions from which the calibration curve data were obtained, and free Cu^{2+} concentrations were measured after equilibrium was

indicated by stable millivolt readings. The change in free Cu^{2+} concentration between the two measurements was calculated and treated as Cu complexed by dissolved organics. The solution pHs were maintained at 6 by adding dilute KOH or HNO_3 solutions using a syringe. The total amount of these adjustments was less than 0.2 % of the solution volume; therefore, no corrections for dilution were made. The whole operation was performed in a black box, since constant light intensity was required.

RESULTS AND DISCUSSION

Characterization of sludge-derived DOC

The total extractable organics in the liquid sludge may be subdivided into three groups:

DOC	71%
humic acids	21%
volatile organics	8%

Here, DOC refers to the organic components that remain in true solution throughout the range of pH from 2 to 12, and it included mainly biochemical compounds and fulvic acids. The organic components that precipitate at pH 2 were arbitrarily termed the humic acids, although other organic substances might be present. Analysis of the water sample in the receiving flask during rotary-vacuum evaporation indicated the presence of volatile organics and the content of the volatile organics was calculated as the difference between total extractable organics and the DOC plus humic acid fractions.

The further fractionation of the DOC material is presented in Fig. 2-1. A significant amount of DOC fell in the < 3500 dalton range, accounting for 38% of the extractable C. The amount of DOC with MW in the 3500-14,000 dalton range only accounted for a very small fraction of the total 8%. Twenty-seven percent of the extractable C was present as organics with molecular weight greater than 14,000 daltons. In the two major molecular weight fractions (MW <3500 and >14,000 daltons), hydrophilic subcomponents were predominant over hydrophobic subcomponents (Fig. 2-1). For DOC in natural water, it is often believed that hydrophilic DOC potentially possesses a higher metal-binding capacity

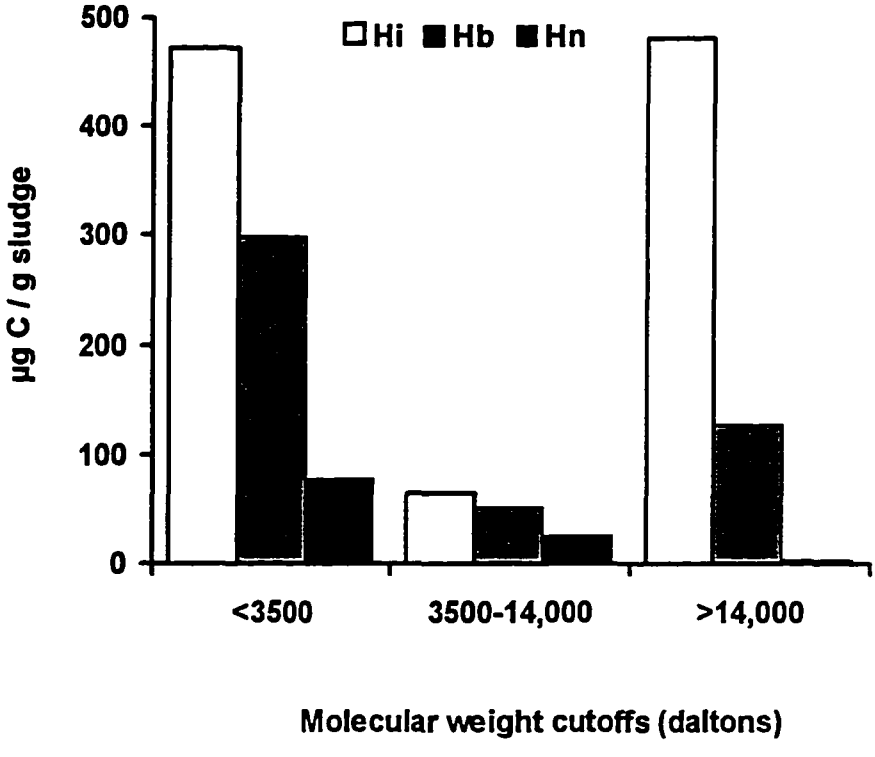


Fig. 2-1. Molecular-weight distribution of sludge-derived DOC
Hi = hydrophilic DOC; Hb = hydrophobic acids;
Hn = hydrophobic neutrals

than the hydrophobic fraction due to its larger proportion of O-containing functional groups. However, very little information is available for DOC obtained from anaerobically digested sludge.

Cu-binding ability of different DOC subcomponents

Determination of Cu-binding ability of EDTA. To verify the procedure developed, the binding ability of a known ligand, ethylendiaminetetraacetate (EDTA), was determined. The results of the complexation capacity determination are summarized in Table 2-1. The ratios of EDTA to complexed Cu illustrate the excellent agreement with the theoretical prediction that EDTA and Cu^{2+} form a 1:1 complex. The free Cu^{2+} concentrations measured with Cu-ISE were also found to be consistent with calculated free Cu^{2+} concentrations by using MINTEQA2 (a computer program for speciation analysis) (Allison et al., 1991). For instance, when the total concentration of 1.22×10^{-4} M Cu was

Table 2-1. Summary of Cu-binding capacity measurements for EDTA (pH 6)

Cu conc. (mole/L) (35 ml)	Cu-ISE Reading (mv)	EDTA addition (ml)	Cu-ISE Reading after EDTA addition	Cu conc. after correction of EDTA volume	Cu bound (mole/L)	EDTA conc. (mole/L)	EDTA / Cu bound
1.57x10-6	121.0	0.13	113.1	1.57x10-6	6.75x10-7	7.39x10-7	1.09
7.87x10-6	139.9	0.69	131.0	7.71x10-6	4.05x10-6	3.86x10-6	0.95
1.57x10-5	148.8	1.00	143.2	1.53x10-5	5.57x10-6	5.55x10-6	1.00
7.85x10-5	169.6	5.00	162.5	6.89x10-5	2.34x10-5	2.50x10-5	1.07
1.57x10-4	178.3	10.00	169.9	1.22x10-4	4.03x10-5	4.44x10-5	1.10

used, and the concentration of EDTA was 4.44 x 10^{-5} M, the measured free Cu^{2+} concentration was 8.2 x 10^{-5} M, which agreed closely with the calculated 7.7 x 10^{-5} M. Other Cu species such as $Cu(OH)^{+}$, and $Cu(OH)_2^{o}$, etc. accounted for less than 0.5 % of the free Cu^{2+}. The data indicate that free Cu^{2+} at equilibrium was the dominant species and could be determined by Cu-ISE accurately, providing a reliable approach for evaluating Cu-binding ability of DOC subcomponents.

Cu-binding ability of DOC with different molecular weights. The analytical data for Cu-binding abilities of the dissolved organics with different molecular weights are presented in Fig. 2-2. As the molecular weights of DOC decreased from > 14,000 to < 3500, the Cu-binding abilities increased significantly. This indicates that low-molecular weight organics have many more binding sites or functional groups compared with high-molecular weight organics. These functional groups need to be further identified in the future research. Information from the literature suggests that the functional groups of carboxylic acid (-COOH), sulfonic acid ($-SO_3H$) and amide ($-CONH_2$) of soluble organic C in sludge are highly involved in Cu-binding, although other functional groups also contribute to the metal binding (Baham et al., 1978; Boyd et al., 1979; Dudley et al., 1987). Although the chemical composition of each molecular-weight range varies with sludge and sampling time, others have found that the larger molecular-weight fractions of DOC, in general, are rich in polysaccharides, polypeptides, anionic detergents and fulvic acids, etc., and low molecular DOC is composed mainly of simple organic acids (Baham et al., 1978; Baham and Sposito, 1983; Dudley et al., 1987). This may explain why the low-molecular weight DOC fraction has more binding sites per mass unit of carbon as compared with the high-molecular weight DOC.

Unlike the complexation between EDTA and Cu^{2+}, the Cu-binding ability of the DOC increased with increasing equilibrium Cu^{2+} concentration, regardless of the molecular weight (Fig. 2-2). Fitch et al. (1986) observed a similar phenomenon for the complexation

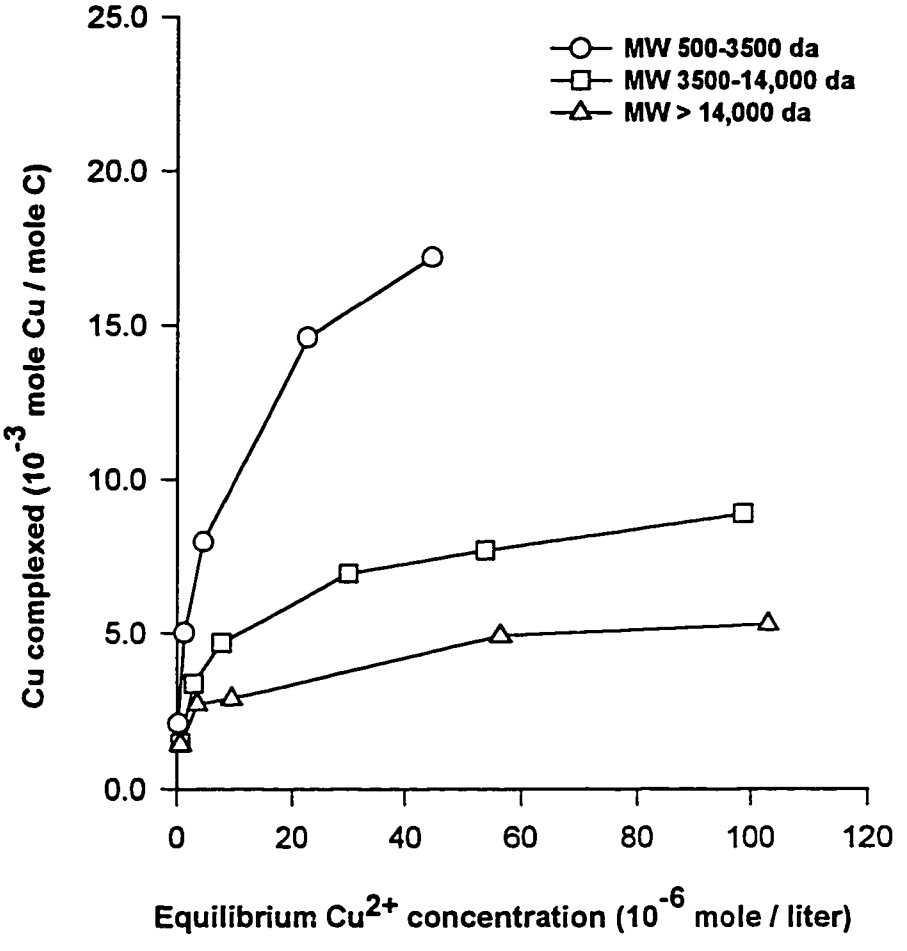
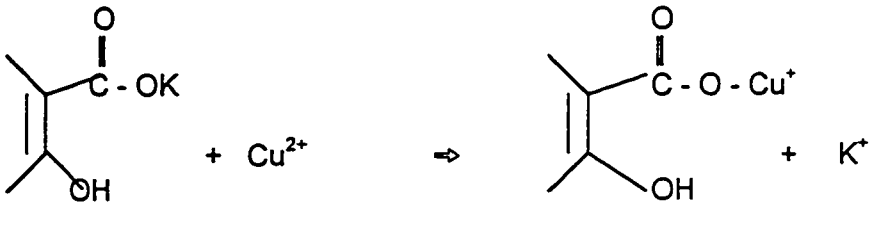


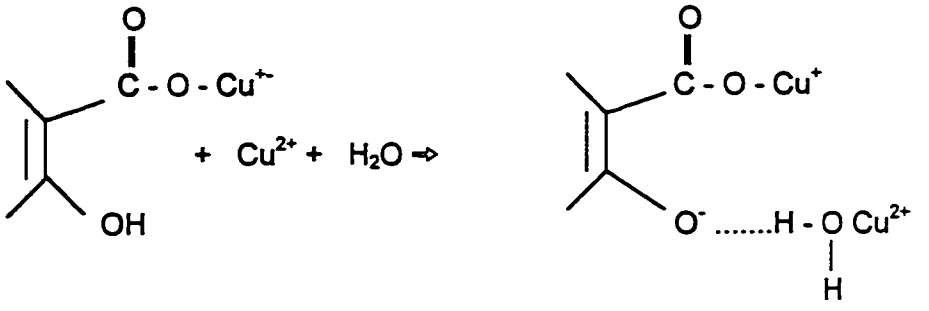
Fig. 2-2 The Cu-binding ability of DOC with different molecular weights

between soil humic acids and Cu^{2+}. They attributed the concentration effect mainly to configurational changes induced by high electrolyte level, and they believed that coiling of the humic acids at higher humic acid and Cu concentrations resulted in increased retention of free Cu^{2+} through physical entrapment. In the present study, such configurational changes are unlikely to have been important because the concentrations of both DOC and Cu^{2+} used were low and the molecular weights of the DOC investigated were much smaller than those of soil humic acids.

Stevenson (1977) hypothesized the formation of 2:1 complexes at low metal / ligand ratios and 1:1 complexes at high metal / ligand ratios when studying the complexation of soil humic acids with transition metal ions such as Cu, Pb, Zn and Cd. He proposed that at low metal / ligand ratios, 2:1 complexes are not formed within the same molecule but are formed by metal ions serving to link two individual organic ligands together to produce chainlike structures. This model of metal binding may partially explain the concentration effect, however, no microscopic evidence is available to verify the mechanism. Another possible explanation for the variable Cu binding ability would be the activation of certain binding sites at higher metal / ligand ratios, sites which would not function as Cu-binding sites at low metal / ligand ratios. At low Cu concentrations only strong binding sites of DOC are likely to form stable complexes or chelates with Cu through covalent bonding, while at higher Cu concentrations more binding sites might complex Cu through weaker bonding such as ion-dipole or hydrogen bonding between binding sites and hydrated shell of Cu^{2+} ions. A schematic explanation can be described as following: at low Cu / DOC ratio:



at high Cu / DOC ratio:



However, the proposed mechanisms are subject to further investigation.

Cu-binding ability of DOC with different polarity. Within the same molecular weight fraction, hydrophilic and hydrophobic components exhibit significant differences in Cu binding. Fig. 2-3 presents the Cu-binding abilities of DOC within the molecular weight range 500-3500 daltons. All three subcomponents were capable of complexing Cu, and the Cu-binding ability of the hydrophilic component was much greater than those of the hydrophobic components (both Hb and Hn). The results were in accordance with the finding of Guggenberger et al. (1994), who reported that heavy metal complexation by hydrophobic acids was much less than that of hydrophilic acids extracted from Spodosol columns. When comparing the Cu-binding abilities among the different subcomponents with higher molecular weights, however, a trend different from that for the lower molecular weight DOC was observed (Fig 2-4, Fig. 2-5). For DOC with molecular weight > 3500 daltons, it was the hydrophobic acid subcomponent that had a much greater Cu-binding ability compared with the hydrophilic subcomponent. The hydrophobic acid fraction prepared in this study is traditionally termed fulvic acids. The most striking feature often reported for fulvic acids is their involvement in metal binding in soil and natural water environments. Although the concentrations of higher-MW hydrophobic acids was lower in

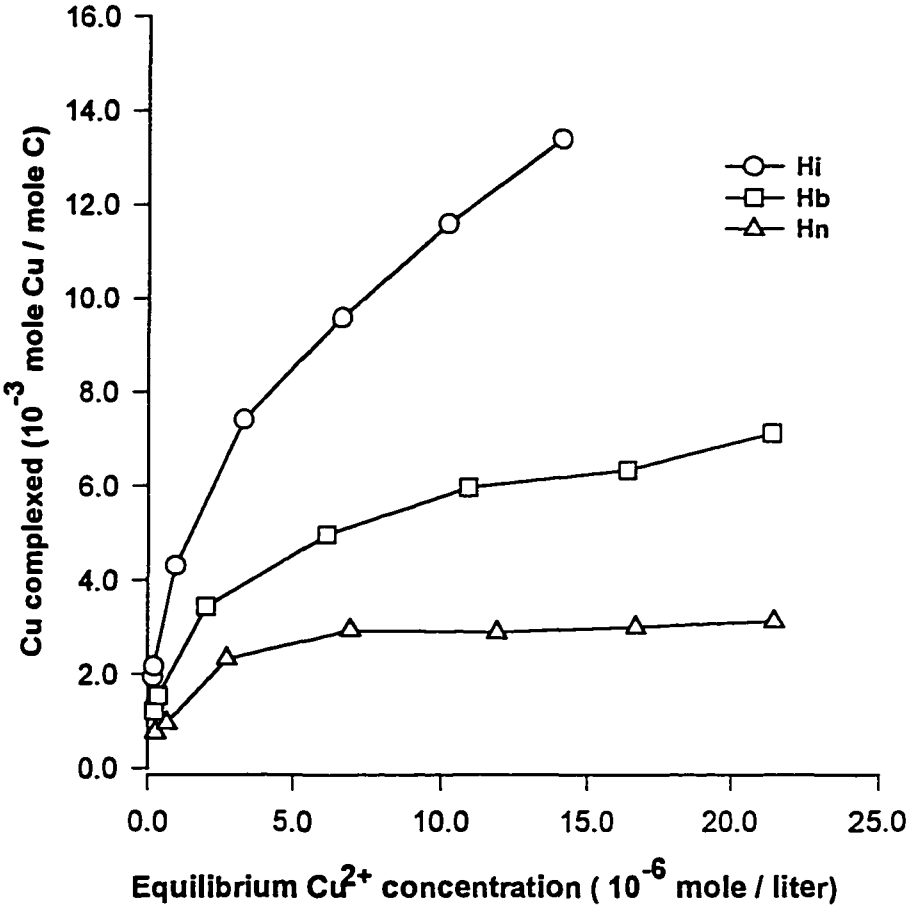


Fig. 2-3 The Cu-binding ability of DOC with MW 500-3500 daltons

Hi = hydrophilic DOC; Hb = hydrophobic acids

Hn = hydrophobic neutrals

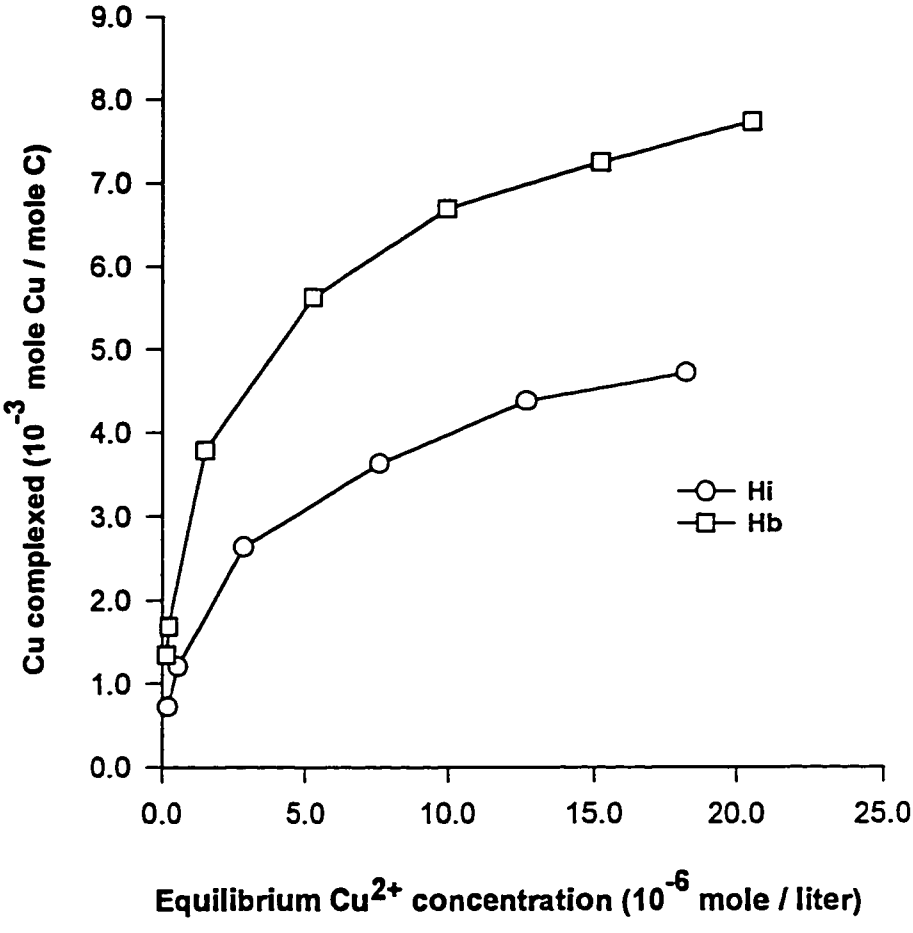


Fig. 2-4 The Cu-binding ability of DOC with MW 3500-14,000 daltons

Hi = hydrophilic DOC; Hb = hydrophobic acids

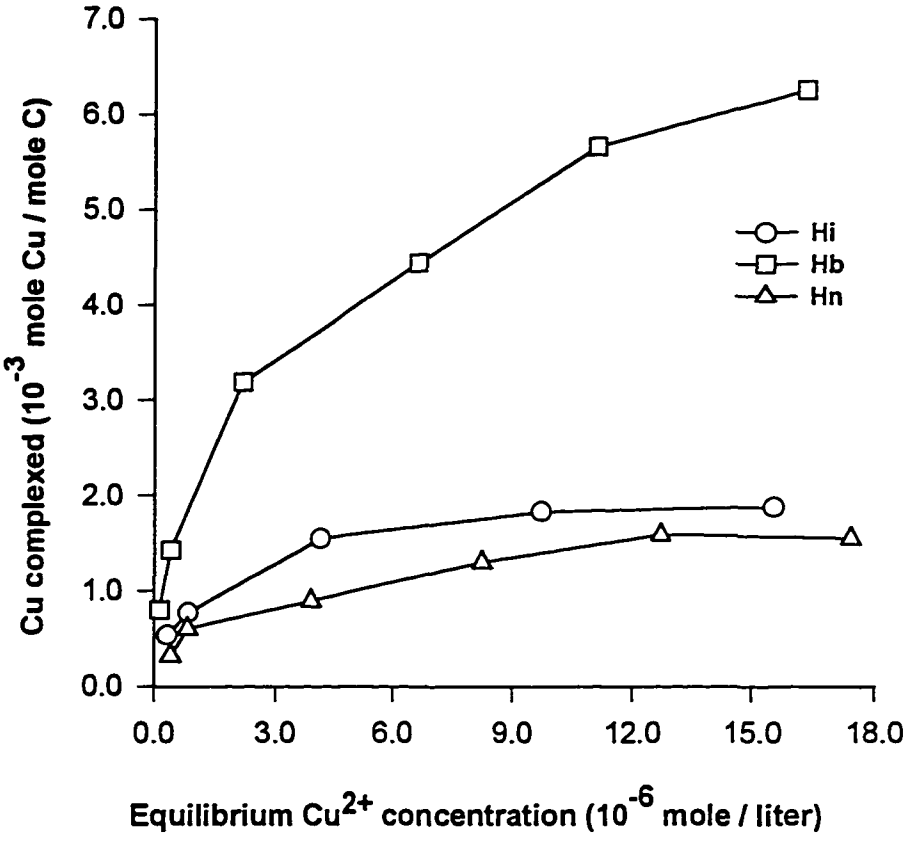


Fig. 2-5 The Cu-binding ability of DOC with MW > 14,000 daltons

Hi = hydrophilic DOC; Hb = hydrophobic acids

Hn = hydrophobic neutrals

the sludge than in the corresponding hydrophilic DOC (Fig. 2-1), these organic acids were the dominating ligands in complexing metal ions. The low Cu-binding ability of the hydrophilic component with large molecular weights suggests that this subcomponent is rich in substances such as polysaccharides, which show high water solubility but low Cu-binding ability.

Comparison of Cu-binding ability of DOC with similar polarity but different molecular weights. The Cu-binding ability of hydrophilic subcomponents with different molecular weight are presented in Fig. 2-6. As molecular weight decreased the Cu-binding ability of the DOC increased dramatically. However, no significant difference in Cu-binding was observed among the hydrophobic acid fractions with different molecular sizes (Fig. 2-7). These results suggest that the nature of the compounds in the hydrophilic fraction changed significantly from high molecular weight to low molecular weight while compounds in the hydrophobic acid fraction varied only in molecular size. The large difference in Cu-binding ability observed in Fig. 2-2, thus, was mainly caused by the difference among the three hydrophilic subcomponents.

Estimation of maximum binding capacity of the DOC subcomponents

The data presented in Fig. 2-2 - Fig. 2-5 can be mathematically treated to fit linear a Langmuir model from which the maximum binding capacity of different DOC subcomponents can be calculated:

$$\frac{C}{X} = \frac{C}{X_m} + \frac{1}{X_m b}$$

where

X = Cu-complexed per unit mass of ligands

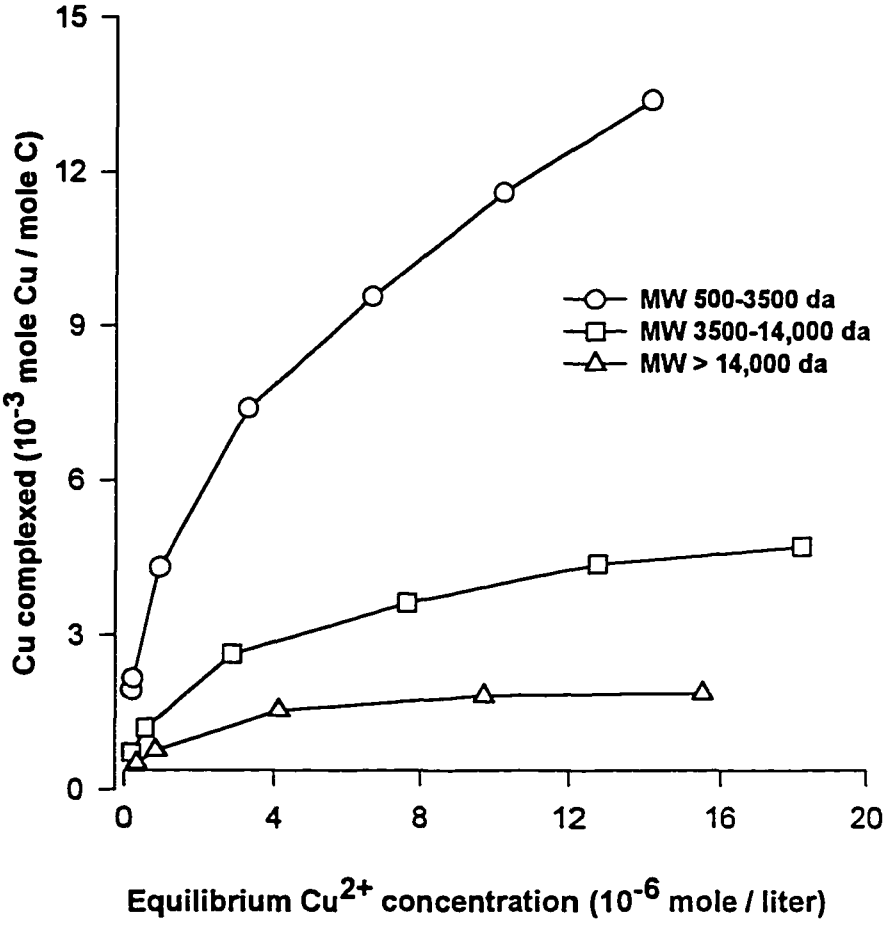


Fig. 2-6 The Cu-binding ability of hydrophilic DOC

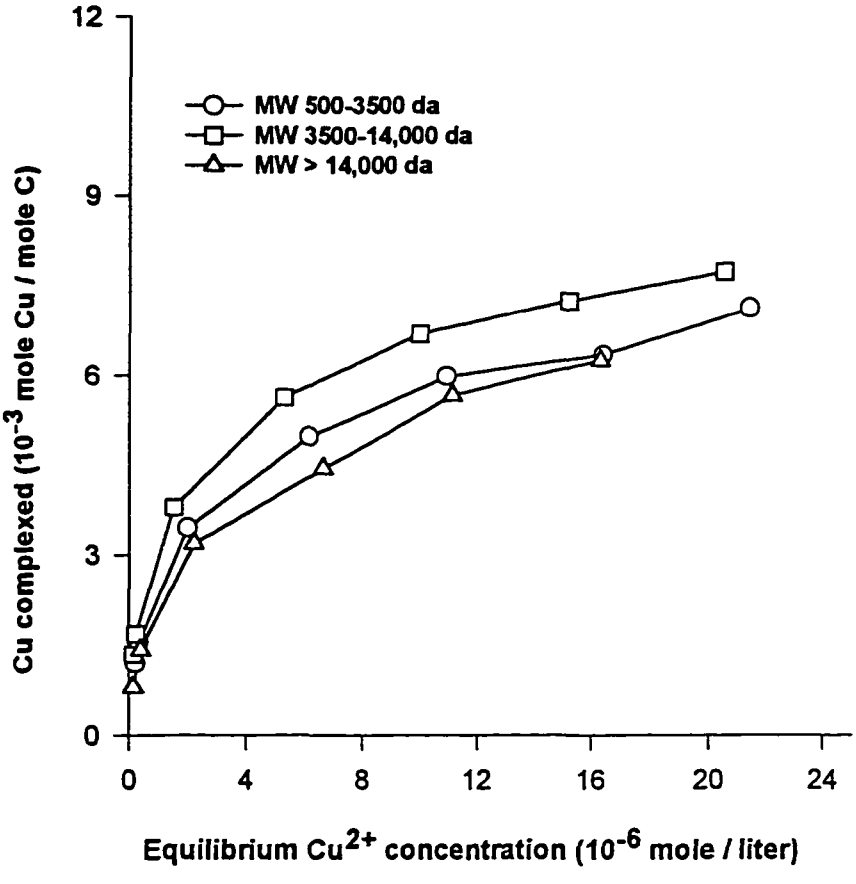


Fig. 2-7 The Cu-binding ability of hydrophobic acids

C = Cu^{2+} concentration at equilibrium

b = a constant indicating the affinity between Cu and the ligand

X_m = maximum binding capacity.

An example is given in Fig. 2-8, which is a linear Langmuir plot for the data of hydrophobic acids with molecular weight within 3500-14,000 daltons. The inverse of the slope is an estimation of the maximum binding capacity of this particular subcomponent.

The calculated maximum capacities for different DOC subcomponents are listed in Table 2-2. The maximum binding capacity varied from 1.85 mmol Cu mol^{-1} DOC for the

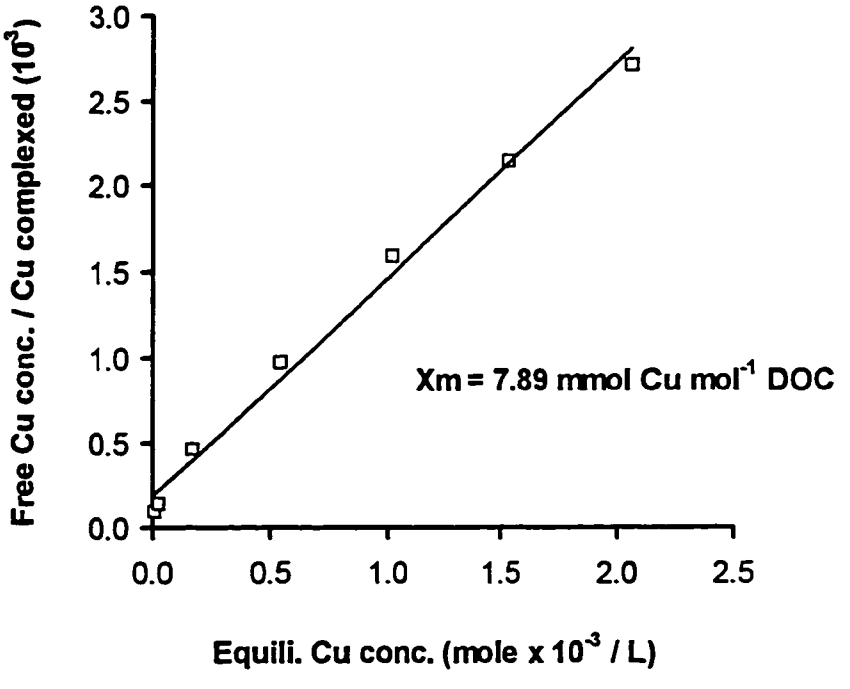


Fig. 2-8. Linear Langmuir plot for hydrophobic acids with MW within 3500-14,000 daltons

hydrophilic subcomponent with molecular weight > 14,000 to 14.3 mmol Cu mol^{-1} DOC for the hydrophilic DOC with molecular weight between 500-3500 daltons, with around 7 mmol Cu mol^{-1} DOC for hydrophobic acids regardless of molecular weights. These values are in very good agreement with others' findings for DOC materials from other sources. For example, Kuiters and Mulder (1992) reported that the Cu-complexing capacities for various litter extracts varied from 9.0 to 10.9 mmol Cu mol^{-1} DOC. According to Guggenberger et al. (1994), Luster et al. (1989) observed a Cu-binding capacity of larch litter extract of 7.56 mmol Cu mol^{-1} DOC.

Oden et al. (1993) reported that the DOC materials from six different sources had different abilities to influence Cu mobility in mineral phase. The contradictory effects of DOC on metal adsorption by soils are also often reported in literature. The present study suggests that DOC materials from different sources will vary in their chemical composition (in terms of molecular sizes and hydrophilicity / hydrophobicity), and therefore vary in metal-binding capacity. Fractionating DOC materials into subcomponents and characterizing their metal-binding abilities may provide important clues to clarify the contradictory results reported in the literature.

Table 2-2. Maximum Cu binding capacity of DOC subcomponents (mmol Cu mol^{-1} DOC)

	MW 500-3500 daltons	MW 3500-14,000 daltons	MW > 14,000 daltons
Hydrophilic fraction	14.30	5.11	1.85
Hydrophobic acids	7.38	7.89	6.71
Hydrophobic neutrals	3.26	n.d.*	1.77

* n.d. = not determined

CONCLUSIONS

Dissolved organics from an anaerobically digested sewage sludge were fractionated by using a combination of molecular weight fractionation and XAD-8 resin chromatography, and the Cu-binding abilities of the subcomponents were further investigated by using a copper ion-selective electrode (Cu-ISE) technique. As dissolved organic carbon (DOC) increased in molecular weight (MW), the Cu-binding ability decreased significantly, indicating that low-molecular weight DOC had many more metal-binding sites compared with high-molecular DOC. Within the same molecular weight fractions, the hydrophilic and the hydrophobic subcomponents also exhibited differences in Cu binding. For the DOC with MW 500-3500 daltons, the hydrophilic subcomponent presented a greater Cu-binding capacity than did the hydrophobic DOC, while the hydrophobic acid subcomponents were the most important components in Cu binding for higher-molecular weight DOC (MW > 3500 daltons). The maximum Cu-binding capacities of different DOC subcomponents, estimated by application of linear Langmuir equation, ranged from 1.85 to 14.30 mmol Cu mol^{-1} DOC, which were in the same magnitude as those reported for other DOC sources in literature.

PART III. THE INFLUENCE OF SLUDGE-DERIVED DISSOLVED ORGANIC CARBON ON COPPER TRANSPORT IN AN AQUIFER MATERIAL

INTRODUCTION

In recent years, the quality of ground water has been a great concern since trace metals and other contaminants originating from agricultural chemicals and sewage sludge that is applied to lands may enter the subsurface environment. For example, Lund et al. (1976) observed that Cu originating from sewage sludge could move 3.5 m below sludge disposal ponds. It has been suggested that presence of high levels of DOC in porous aquifers will accelerate trace metal transport in the subsurface environment (McCarthy and Zachara, 1989). Heavy land application of certain sewage sludges introduces not only potentially hazardous trace metals but also mobile organic materials into soils (Section I). Although much of the potentially mobile organic material undergoes microbial transformation near the soil surface, some fraction of it may move down to shallow aquifers, particularly through open soil channels and cracks. Due to the metal-binding ability of sludge-derived DOC, it is important to investigate the influence of DOC on trace metal movement in aquifer material in order to provide information to assure a safe land disposal of municipal sewage sludge.

The transport of naturally occurring DOC and its subcomponents in aquifer materials has been studied at the scale of laboratory columns as well as at the field-scale (e.g., Dunnivant et al., 1992a; Jardine et al., 1992; McCarthy et al., 1993). A general conclusion that may be drawn from these studies is that low-molecular weight, hydrophilic DOC subcomponents are highly mobile and are assumed to facilitate metal transport in aquifer material (Dunnivant et al., 1992a; McCarthy et al., 1993). However, studies on metal ion transport in the presence of DOC are contradictory in the literature. Dunnivant et al. (1992b) demonstrated an increase in Cd migration in the presence of stream-derived

DOC, while Oden et al. (1993) observed a decrease in Cu mobility in the presence of DOC from a number of sources. Giusquiani et al. (1992) reported an increase in mobility for several heavy metals in soils amended with urban waste compost, however they demonstrated that the DOC in the compost had a limited influence on the metal mobilities. Thus, the assumption that DOC facilitates heavy metal movement in the subsurface needs to be further examined.

Copper was chosen as the model metal ion in this study, although it is considered a low-mobility element in most soil environments. The rationale was that

a) it strongly complexes with most organic ligands (McBride, 1994), allowing the role of DOC to be evaluated effectively;

b) it is a potentially harmful trace metal and often the first element to limit land application of sewage sludges (Alloway, 1990; McBride, 1994).

The objectives of this study were, by using laboratory columns, (i) to investigate the transport behavior of Cu, sludge-derived DOC and DOC subcomponents; (ii) to examine the influence of the DOC subcomponents on Cu mobility in an aquifer material; and (iii) to determine the possible effect of Fe and Mn oxides on the mobility of Cu or DOC in the aquifer material.

MATERIALS AND METHODS

Aquifer material

Preparation of aquifer material. The aquifer material was collected from a sewage sludge-amended experimental field near the City of Ames Water Pollution Control Facility, IA. The material was taken 230 cm below the surface, air-dried and passed through a plastic sieve with 600-μm cutoff (No. 30). The material with diameter greater than 600 μm was excluded since larger particles would cause packing difficulty in small chromatography columns used for the transport study. In order to investigate the effect of Fe and Mn oxides on DOC or Cu transport, a portion of the material was further treated with citrate-bicarbonate-dithionite (CBD) to remove Fe and Mn oxides by the procedure developed by Franzmeier et al. (1977). The treated material was washed extensively with 0.05 M KNO_3 until free citrate had leached, and then the material was air-dried before use.

Characterization of the aquifer material. The particle size distribution of the aquifer material was determined by the pipette technique (Walter et al., 1978). The Fe and Mn contents were measured by CBD extraction of Franzmeier et al. (1977). The pH of the aquifer material was measured at the ratio of 1:1 of solid to water, and total carbon was determined by high-temperature combustion (Nelson and Sommers, 1982).

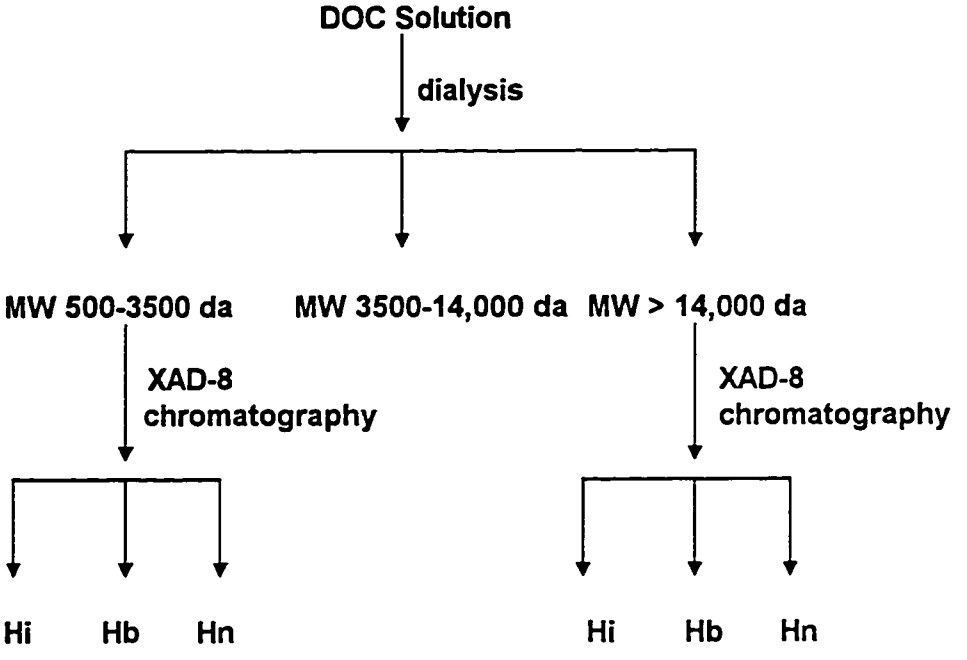
The determination of point of zero charge (PZC) was carried out by an equilibrium approach. To each of three sets of beakers, 4 g of the aquifer material were added with 10 ml of electrolyte solution of 0.02, 0.2, and 2.0 M NaCl, respectively. Then, small increments of dilute acid or base (0.2 M HCl or 0.2 M NaOH) were added to each set of the beakers and the final volume in each beaker was adjusted to 20 ml with distilled-deionized

water to maintain the final electrolyte concentrations at 0.01, 0.1, and 1.0 mole L^{-1} NaCl. The blanks containing no aquifer material but having the same salt and acid or base concentrations were prepared in the same way. After a 4-day equilibration, the pHs of the supernatants in the beakers were measured, and the amounts of H^+ or OH^- adsorbed by the aquifer material at any given pH value were calculated from the amount of HCl or NaOH added to the suspensions minus the amount of acid or base required to bring the same volume and the same concentration of NaCl solution, without aquifer material, to the same pH (Van Raij and Peech, 1972).

The Cu-adsorbing capacity of the aquifer material was determined by a batch equilibrium approach. The aquifer samples of 1.000 g were accurately weighed into 50-ml Teflon centrifuge tubes. Aliquots of 30 ml of Cu^{2+} solution ranging from 3.14×10^{-5} to 3.14×10^{-4} mol L^{-1}, made up in 0.025 M KNO_3 at pH 6, were added to the tubes. The aquifer mixtures were shaken on a reciprocal shaker for 16 hr. The suspensions were centrifuged at 7600 rpm for 10 min and then filtered through Whatman No. 40 ash-free filters. The Cu concentrations in the equilibrium solutions were determined by using an atomic absorption spectrophotometer. The data obtained were fit to the Langmuir equation, and the maximum adsorbing capacity was evaluated (see Part II).

Preparation of DOC subcomponents

The DOC solutions used in this study were extracted from anaerobically digested sewage sludge collected from the City of Ames Water Pollution Control Facility, IA. The DOC solution was fractionated and isolated according to the flow chart shown in Fig.3-1. The procedures for the fractionation and isolation were reported in detail in Part II. The two most abundant molecular weight (MW) fractions, MW 500-3500 and MW > 14,000 daltons,



Hi = hydrophilic fraction; Hb = hydrophobic acids

Hn = hydrophobic neutra

Fig. 3-1 Flow chart of hydrophilic / hydrophobic seperation

were chosen for the transport study. For both MW fractions, the total hydrophilic and hydrophobic acid subcomponents were used to perform both DOC transport and DOC / Cu co-transport. The hydrophobic neutral subcomponents were used to perform only DOC transport experiments because of the difficulty in sample collection due to their low concentration levels in the sewage sludge.

Column experimental design

A schematic column experimental design is shown in Fig. 3-2. Glass chromatography columns (1.5 cm i.d. x 10 cm long) were used for the column transport study. Input solution in a solution reservoir was fed to the column by a peristaltic pump (Wiz, ISCO). The effluent was collected by a fraction collector (Retriever II, ISCO).

Aquifer columns were dry-packed to a uniform bulk density of 1.45 g / cm^3 (with porosity of 0.45 and total pore volume of 7.95 cm^3), and wetted upward with 0.025 M $KClO_4$ at 0.5 ml / min by using a peristaltic pump. The columns were saturated slowly over 3 days to remove air pockets resulting from the dry-packing technique. The breakthrough curves of a conservative tracer (Cl^-) were performed for evaluation of the column transport features. Then, the aquifer columns were periodically eluted with dilute acid to bring the effluent pH to around 6.6-6.7 before each transport experiment in order to minimize complications due to Cu speciation.

The transport of DOC or pre-equilibriated DOC / Cu (II) solutions was investigated by applying a continuous input solution to the aquifer column (Darcy's flux = 0.0047 cm s^{-1}). The initial DOC or Cu^{2+} concentrations in the solutions were approximately 30 µg C ml^{-1} (ranging from 29.5 to 31.8 µg C ml^{-1}) for DOC and 5 µg Cu ml^{-1} (ranging from 4.6 - to 4.8 µg Cu ml^{-1}) for Cu^{2+}. These DOC or Cu concentrations were arbitrarily chosen for the

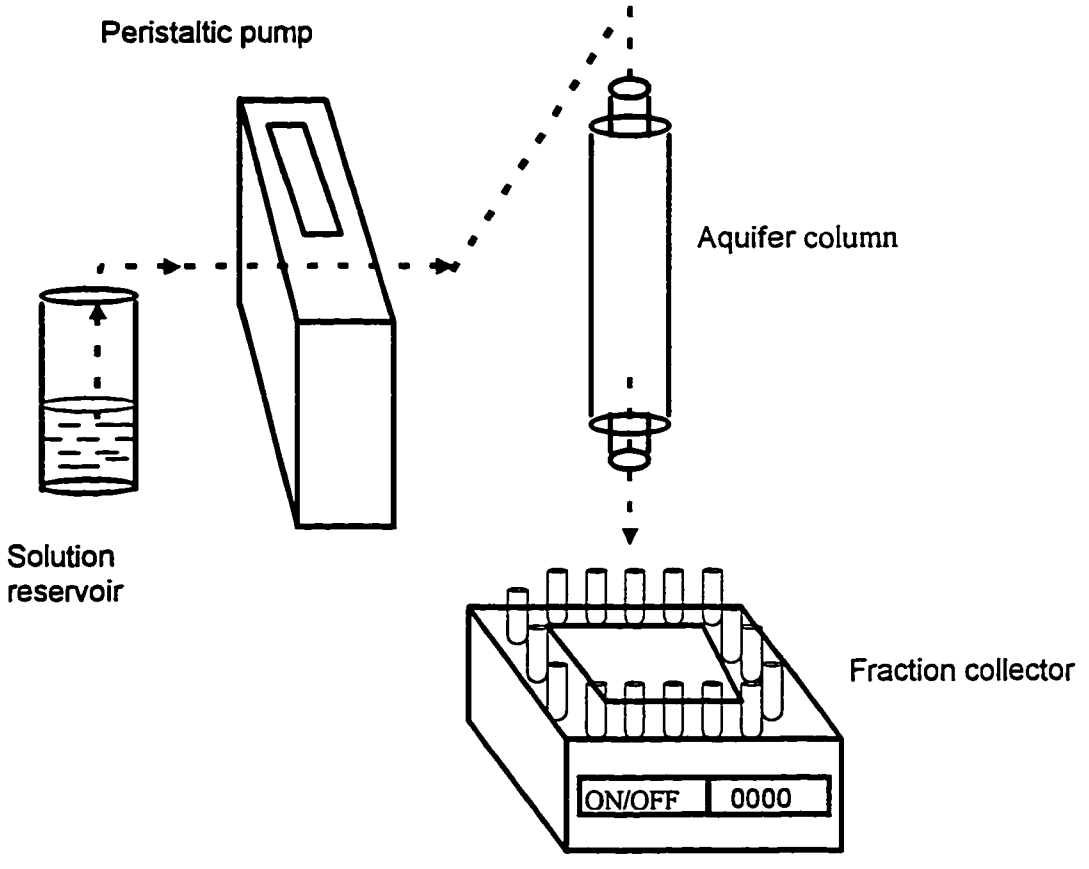


Fig. 3-2 A schematic diagram of the column design

convenience of experimental design, although they were possibly higher than those often observed in aquifer environments. The co-transport of Na_2EDTA / Cu (II) solution (containing 32 μg C ml^{-1} and 5.2 μg Cu ml^{-1}) was also investigated in order to provide a comparison of the influence of a well defined organic ligand and sludge-derived organic ligands on Cu mobility in the aquifer medium. All the solutions contained 0.025 M KNO_3 and 0.0005 % NaN_3 (w/ w) and were adjusted to pH 6.2. The NaN_3 was used to prevent microbial alteration of the DOC during column experiments, and the KNO_3 was used to maintain a constant ionic strength and to prevent any dispersion of clay particles from the aquifer columns. The total Cu(II) concentrations in the effluents were determined by using an atomic absorption spectrophotometer, and DOC was measured with a Shimadzu carbon analyzer.

RESULTS AND DISCUSSION

The physical and chemical characteristics of the aquifer material

Some of the basic characteristics of the aquifer material are listed in Table 3-1. The material was high in sand content and low in clay content. It was relatively rich in Fe and Mn oxides and hydroxides but poor in organic matter. The pH of the material was close to its point of zero charge (PZC) (Table 3-1 and Fig. 3-3b).

Table 3-1. The basic properties of the aquifer material

Physical	Sand (53-600 μm)	97.0 %
	Silt (2-53 μm)	0.4 %
	Clay (<2 μm)	2.6 %
Chemical	Dithionite-extractable Fe	7.41 mg / g
	Dithionite-extractable Mn	1.92 mg / g
	Total C	0.30 mg / g
	pH	7.4
	Point of zero charge	7.6
	Maximum Cu-adsorbing capacity	536 μg Cu g^{-1}

The point of zero charge has been defined slightly differently by many investigators. Hendershot and Lavkulich (1978) defined PZC as "the pH at which the net total charge on the solid phase is zero, whether the charge arises from pH-independent charge associated with isomorphous substitution or from pH-dependent charge associated with hydroxylated oxide or organic matter surfaces." Owing to the permanent charge of silicate clays and the presence of organic matter, the PZC for many soils are in the range of 3.5-4.5, much lower than those of pure Fe and Al oxides (ranging from 7 to 9) (McBride, 1994). The point of

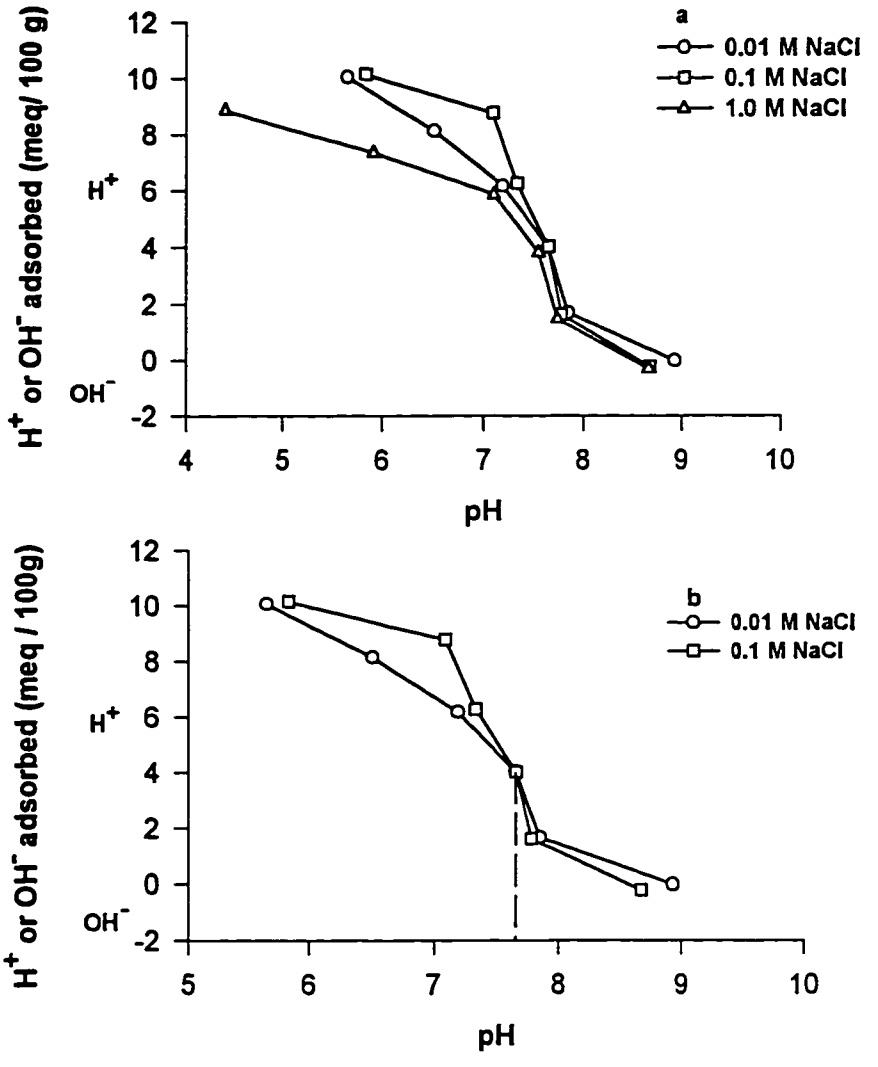


Fig. 3-3 The PZC determination of the aquifer material

a. = under three electrolyte concentrations

b = under two low electrolyte concentrations

zero charge approaches the natural pH of the soil only when the accumulation of the sesquioxides is extensive and the contribution of pH -independent charges is relatively insignificant (Hendershot and Lavkulich 1978). In the present study, the PZC of the aquifer material near its natural pH indicates that Fe oxides and hydroxides were the very important components of the aquifer material and would provide a significant portion of active sites for Cu or DOC to interact with. As shown in Fig. 3-3a, the curves at concentrations of 0.01 M and 0.1 M NaCl intersected at pH 7.6, and the one at 1.0 M NaCl failed to achieve crossover at the same pH value. Hendershot and Lavkulich (1978) reported the same observation for Typic Ferrudalf B horizons. This phenomenon might be related to the presence of permanent charges of silicate clays or to negative charges originating from Mn oxides. McBride (1994) pointed out that indifferent salts suppress H^+ adsorption on permanently negative sites at high ionic strength. Hendershot and Lavkulich (1978) questioned the ordering of Na^+ and H^+ in the double layer at high ionic strength. However the exact mechanism is not known.

The transport of Cu in aquifer material is largely dependent upon the adsorption characteristics of the material and its components. The Cu adsorption isotherms of the original and oxide-free material (CBD-treated) are presented in Fig. 3-4. The untreated aquifer material possessed a great potential to adsorb Cu ions, and the maximum Cu-adsorbing capacity estimated from the Langmuir equation was as high as 536 $\mu g\ g^{-1}$ material. The Cu-adsorbing sites in the untreated aquifer material probably originated from silicate clays, Fe and Mn oxides or hydroxides and organic matter. Since the aquifer material only contained 0.03% total carbon, the contribution of organic matter to the Cu adsorbing capacity was expected to be limited. If one assumes that only phyllosilicate clays and Fe and Mn oxides or hydroxides contributed to the adsorbing sites, silicate clays

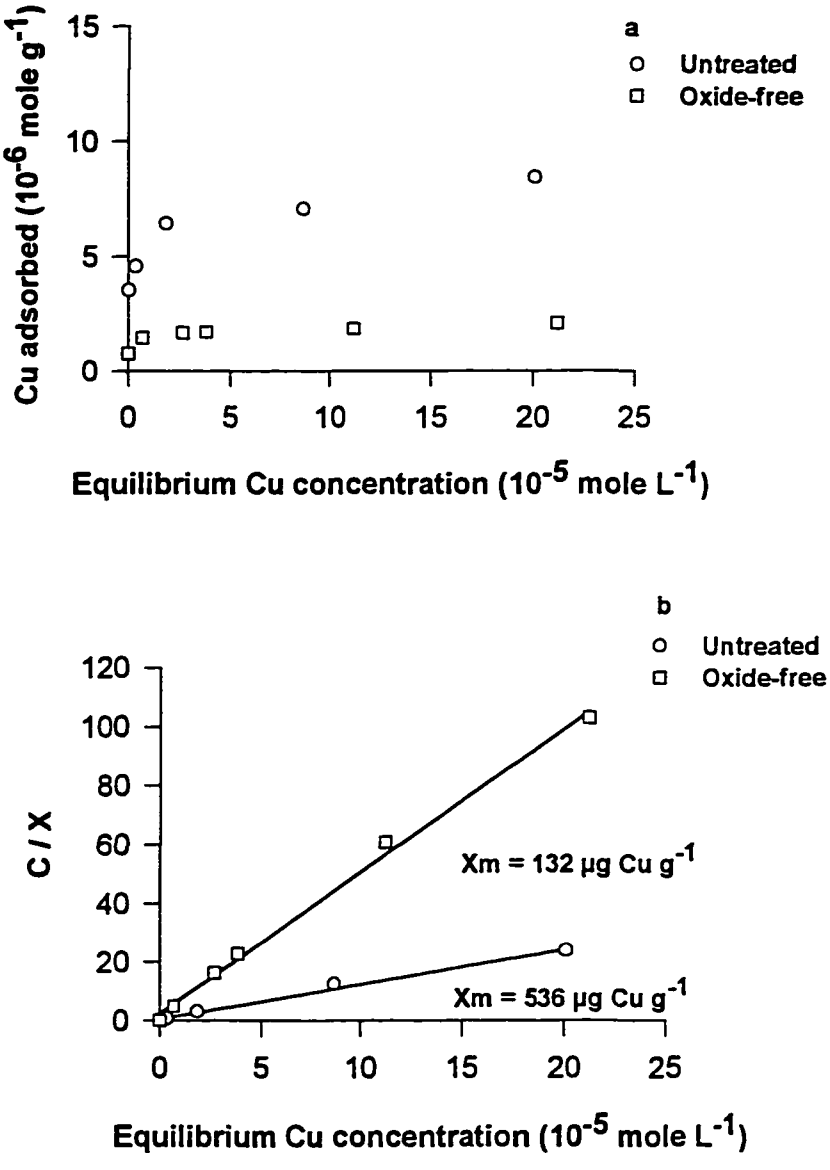


Fig. 3-4 Cu adsorption isotherm of the aquifer material

a = amount of Cu adsorbed vs. equilibrium Cu concentration

b = linear Langmuir plot

were responsible approximately 132 μg Cu g^{-1} (oxide-free material in Fig. 3-4), accounting for 25 % of the total Cu-adsorbing capacity. The remaining 75 % of the adsorption sites were created by Fe and Mn oxides and hydroxides in the aquifer material. The results are consistent with McLaren and Crawford's observations that Fe and Mn oxides have a much greater Cu-adsorbing capacity compared with silicate clays (13-130 times) (McLaren and Crawford, 1973 and 1974).

Three types of adsorption mechanisms may be involved:

i) retention by cation exchange sites of silicate clays;

ii) possible entrapment in the internal structures of Mn oxides or hydroxides (McKenzie (1980) reported a penetration of Cu into the interlayer regions of Mn oxides.); or

iii) chemisorption onto the surface of the Fe and Mn oxides or hydroxides (Cu has a tendency to be specifically adsorbed by forming metal oxide-O-Cu through covalent bonding with the surfaces of Fe and Mn oxides, and the adsorption can occur below the PZCs of these oxides.).

Since the solution pHs at equilibrium were around 6, the sorption of Cu by the aquifer material occurred at a pH much lower than the PZC of the material, when the surface of the aquifer solid phase was carrying a net positive charge. Thus, the sorption process was believed to proceed predominantly through chemisorption against electrostatic repulsion by the surface. A detailed discussion of the mechanisms is included in the Literature Review section of this dissertation.

Transport of sludge-derived DOC and its subcomponents

Before investigating the transport of the DOC, the physical characteristics of the aquifer columns were evaluated with the conservative tracer Cl^-. A representative Cl^- BTC is shown in Fig. 3-5, where C is the concentration of Cl^- found in the effluent and C_o is the initial concentration of Cl^- in the influent. V represents the pore volume of effluent collected and V_o represents the volume of the porous medium occupied by the liquid phase. The parameters obtained from the Cl^- BTC can be applied to estimate the Peclet number of the column, an approach often used to evaluate flow characteristics of the column. With Peclet number greater than 35, preferential flow is insignificant during solute transport (Dunnivant et al., 1992a). This allows the chemical reactions that affect transport to be evaluated. Peclet numbers can be calculated from the following equation:

$$P = V L / D$$

where V = mean pore-water velocity (m / sec)

L = length of aquifer column (m)

D = diffusion - dispersion coefficient (m^2 / sec)

Since D can be evaluated by $D = VL / 4\pi R^2 S^2$, thus

$$P = 4\pi R^2 S^2,$$

where R is the retardation factor (equal to the relative pore volume at $C / C_o = 0.5$), and S represents the slope of a BTC at R pore volume. In the present study, both R and S were obtained graphically. This approach was confirmed to be consistent with CXTFIT prediction (a computer program for transport parameters) (e.g, Fig. 3-5) (Parker and Van Genuchten, 1984). The estimated Peclet numbers for the aquifer columns of this study ranged from 42.9 to 102.4, with an average of 69.3. Thus, the complication of preferential flow was negligible in these columns.

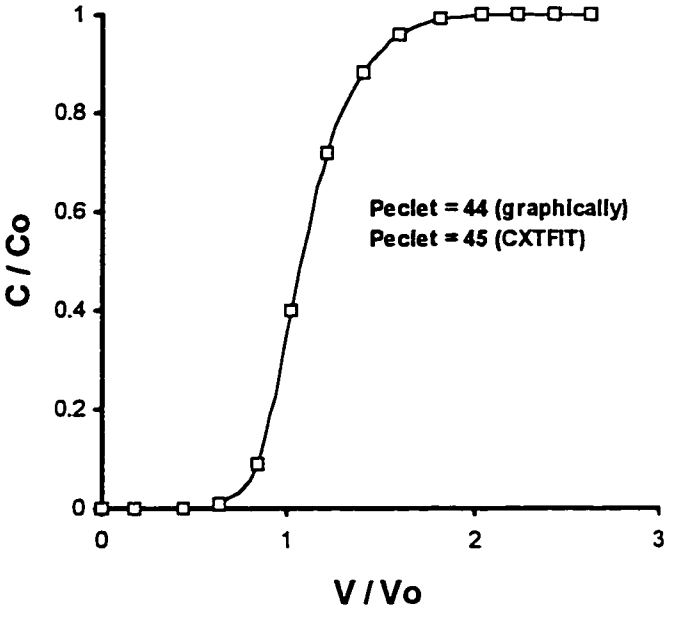


Fig. 3-5 A BTC of Cl- in the column material

The retardation factor is an important parameter and can also be defined as:

$$R = 1 + \rho_b K_d / \Theta$$

Where ρ_b is bulk density, and Θ is volumetric water content. K_d is simply the ratio of solute sorbed to solute in solution. For nonsorbable solutes, the retardation factor is expected to be unity. Large retardation factors can mean that the solutes are strongly adsorbed by the solid phases and their transport is likely to be retarded.

Transport of DOC with different molecular weights. Fig. 3-6 presents the breakthrough curves for DOC of two molecular weight fractions, MW 500-3500 and MW > 14,000 daltons. The vertical axis represents relative DOC concentration, C / C_o, where C is the effluent concentration and C_o is the influent DOC concentration. The horizontal axis represents pore volumes of solution passed through each column. These breakthrough curves feature an initial rapid increase in DOC concentration, followed by extended tailing. The effluent concentrations did not reach the influent concentrations even after approximately 16 pore volumes passed when the input of DOC was terminated. The tailing is an indication of slow adsorption of the DOC to the aquifer material. The MW 500-3500 fraction was sorbed less strongly than the MW > 14,000 fraction. At a relative pore volume of 2, the MW 500-3500 fraction reached 70% of its input concentration, whereas the MW > 14,000 fraction reached 50% of its initial concentration. This difference occurred through the entire experiment, indicating a preferential adsorption of DOC with larger molecular weights. Dissolved organic compounds with lower molecular weights had a smaller tendency to be adsorbed and were more mobile in the aquifer medium. The DOC with smaller molecular weights was also observed to be more mobile than the DOC with high molecular weights in a field study by McCarthy et al. (1993). Compared with high MW DOC, low-MW DOC has higher metal-binding capacity (Part II), higher mobility and less tendency

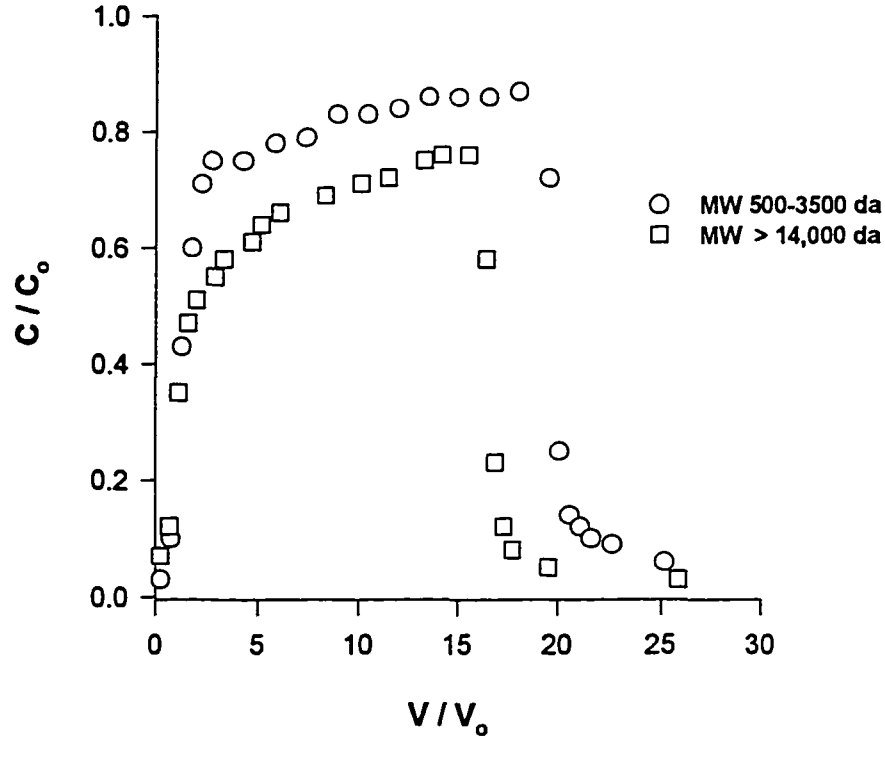


Fig. 3-6 The BTCs of DOC with different molecular weights

to be adsorbed. Naturally, it was expected that this DOC subcomponent will have greater potential to accelerate metal migration in the aquifer matrix. However, further investigation has determined that this statement is not completely true.

After DOC inputs were terminated, 0.025 M $KClO_4$ solutions were pumped through the columns to desorb the adsorbed DOC. A rapid decrease in DOC concentrations was observed for both molecular weight fractions (Fig. 3-6). This suggested that the adsorbed DOC was strongly retained by the aquifer material. Similar observations were also reported by Dunnivant et al. (1992a) and Gu et al. (1994) on the desorption of stream- or peat- derived DOC by an aquifer material and an Fe oxide.

The transport of DOC subcomponents with different polarity. The mobilities of the DOC subcomponents with different hydrophilicity / hydrophobicity properties are presented in Fig. 3-7 for MW 500 - 3500 daltons and in Fig. 3-8 for MW > 14,000 daltons. The mobilities of these subcomponents followed the order of total hydrophilic DOC > hydrophobic acids > hydrophobic neutrals. This phenomenon was more pronounced for DOC with MW > 14,000 daltons. For this MW fraction, the effluent concentrations of the total hydrophilic, hydrophobic acid and hydrophobic neutral subcomponents reached approximately 66, 20 and 10% of their influent concentrations at a relative pore volume of 2 , respectively. The results indicate that hydrophobic DOC, particularly the hydrophobic neutral fraction, was preferentially adsorbed by the aquifer material relative to hydrophilic organic compounds.

In general, the adsorption mechanisms of DOC by aluminosilicates, oxides and hydroxides of Fe and Mn may include 1) non-specific anion exchange, 2) specific ligand exchange, 3) hydrogen bonding, 4) cation bridging, and 5) hydrophobic interaction. Detailed discussion of these mechanisms is found in the Literature Review section of this

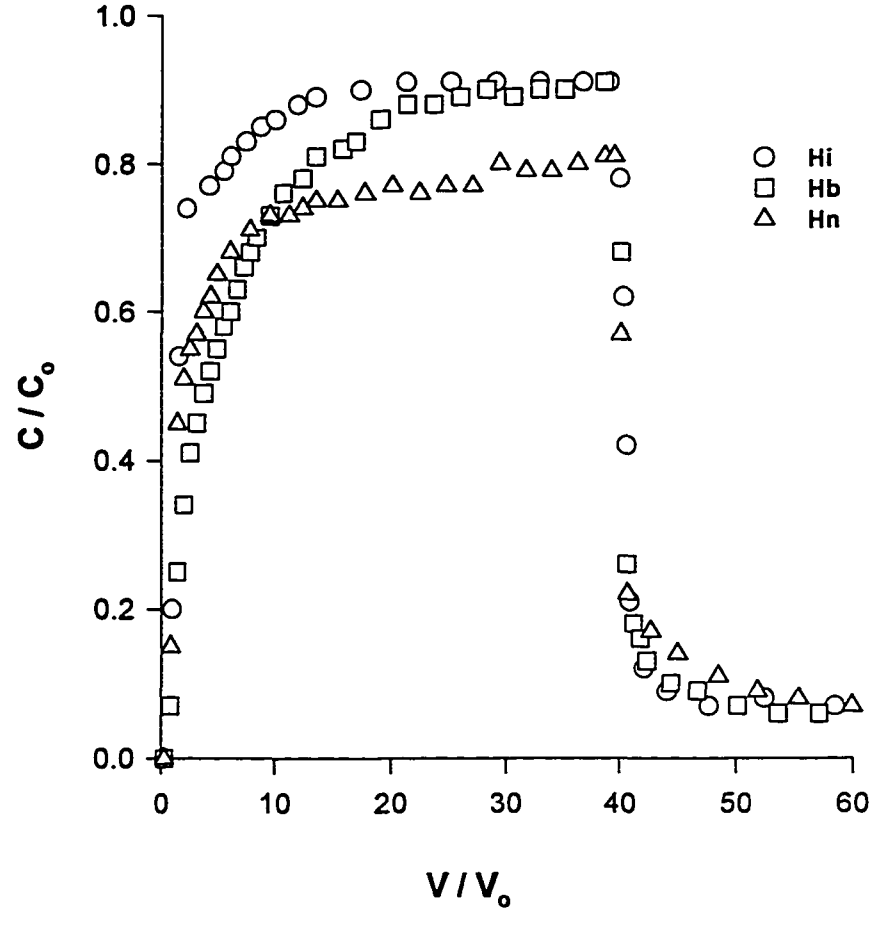


Fig. 3-7 The BTCs of DOC subcomponents with MW 500-3500 daltons

Hi = hydrophilic DOC; Hb = hydrophobic acids

Hn = hydrophobic neutrals

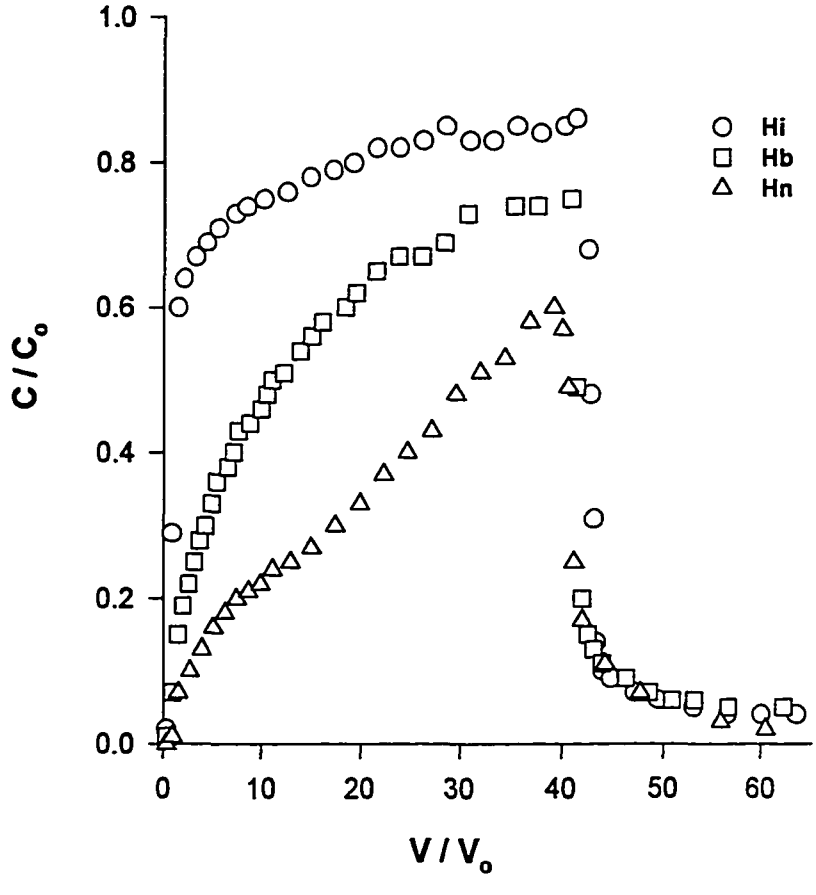


Fig. 3-8 The BTCs of DOC subcomponents with MW > 14,000 daltons

Hi = hydrophilic DOC; Hb = hydrophobic acids

Hn = hydrophobic neutrals

thesis. The adsorption of peat-derived DOC on Fe oxides conducted by Gu et al. (1994) indicated that specific ligand exchange played a dominant role in DOC adsorption. On the other hand, Jardine et al. (1989) and Baham and Sposito (1994) demonstrated that the primary adsorption mechanism for peat-derived or sludge-derived DOC for various soil components was physical adsorption caused by favorable entropy changes (i.e., hydrophobic interaction). In the present study, the preferential adsorption of large MW DOC (Fig. 3-6) and hydrophobic subcomponents (Fig. 3-7 and Fig. 3-8) suggests that hydrophobic attraction played a significant role in retarding the transport of various DOC in the aquifer material.

The influence of Fe and Mn oxides on DOC transport. It has been reported that Fe and Mn oxides or hydroxides may retain up to 70% of the total adsorbed DOC in some soils (Jardine et al., 1989). The effects of the sesquioxides in the aquifer material of the present study on retardation of three DOC subcomponents were evaluated by comparing the transport behaviors of DOC in dithionite-treated material with those in untreated material, and the results are presented in Fig. 3-9 and Fig. 3-10. Surprisingly, the oxides and hydroxides present in the aquifer material showed a selectivity in retarding the transport of the DOC subcomponents. For DOC subcomponents of the same polarity fraction, the oxides selectively impeded the mobility of the DOC with higher molecular weights (Fig. 3-9). The breakthrough behavior of hydrophilic DOC with MW 500-3500 daltons was not affected by the oxide removal (Fig. 3-9a). At a relative pore volume of 10, the relative concentration of hydrophilic DOC with MW > 14,000 daltons in the effluent was 90% in oxide-free material, whereas that of the same fraction was only 71% in untreated material (Fig. 3-9b). For the highly mobile, low MW DOC (MW 500-3500 daltons), the oxides slightly retarded the mobility of the hydrophobic DOC (Fig. 3-10 b) and had little

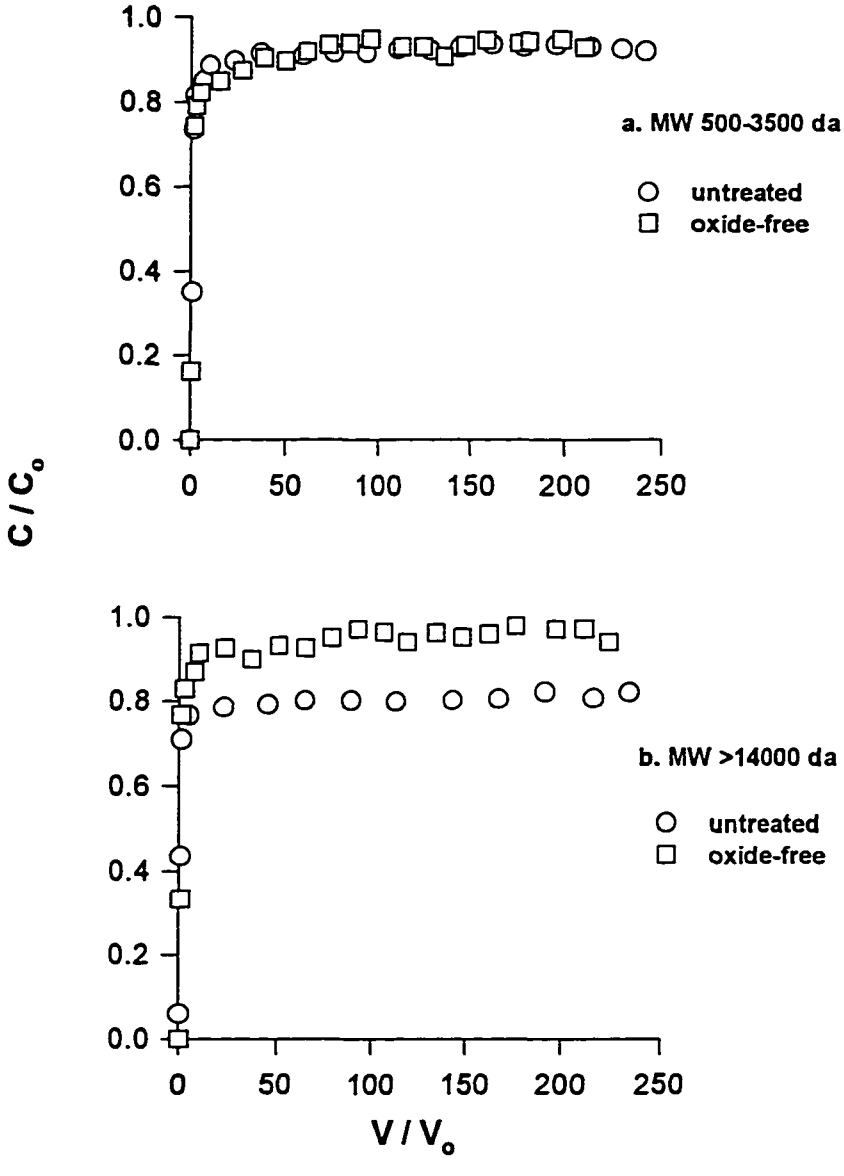


Fig. 3-9 Effect of Fe- and Mn- oxide removal on hydrophilic DOC transport

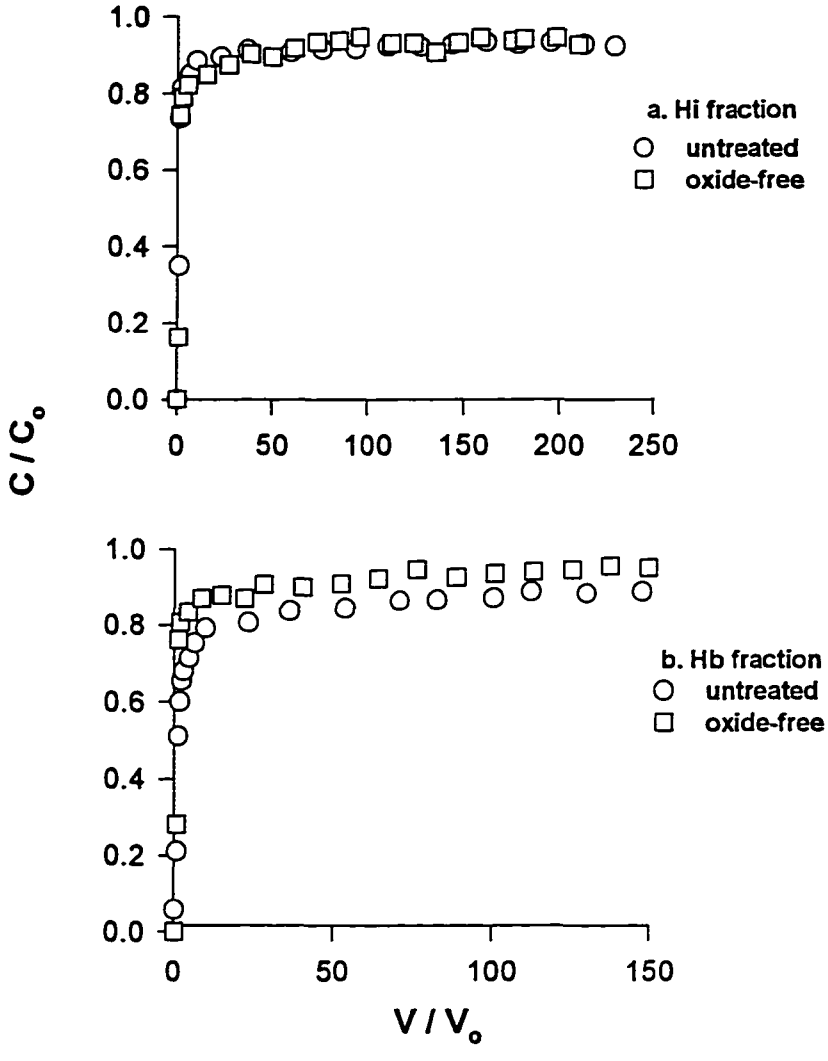


Fig. 3-10 Effect of Fe- and Mn- oxide removal on the transport of DOC with MW 500-3500 daltons

influence on that of hydrophilic compounds (Fig. 3-10 a). This selectivity suggests that the oxides may provide hydrophobic surfaces for hydrophobic DOC or high-molecular-weight DOC to interact with. However, Fe and Mn oxides are often believed to act as hydrophilic surfaces since these surfaces are hydroxylated (McBride, 1994). The possible mechanisms for the observed selectivity may be related to the interaction between positively charged sites on the oxide surfaces and the organic ligands, followed by hydrophobic partitioning. Since the Fe oxide surfaces probably carried a net positive charge under the experimental conditions (effluent pH < PZC), some negatively charged organic ligands could be strongly adsorbed by the surface through electrostatic force. Adsorption of a layer of large organic polymers or hydrophobic DOC through electrostatic interaction would convert the hydrophilic surface of the oxides into hydrophobic surface and more large organic molecules or hydrophobic DOC could be further partitioned ("dissolved") into the adsorbed organic layer. This effect would not be significant for low-MW, hydrophilic DOC due to its high affinity for and solubility in water. After the oxides were removed by treatment with dithionite, the positively charged sites disappeared, hydrophobic partitioning became less important, and more DOC with large molecular weight or high hydrophobicity could be transported through the aquifer medium.

Transport of Cu (II) in the aquifer columns

The transport of Cu in an aquifer matrix is largely controlled by Cu interactions with the solid phase. This is seen in Fig. 3-11 which presents the BTCs of Cu in the aquifer columns with or without oxides removed.

As shown in Fig. 3-4, the untreated aquifer material possessed a large capacity to adsorb Cu ions with a maximum adsorbing capacity of 536 $\mu g\ g^{-1}$ material. Consequently,

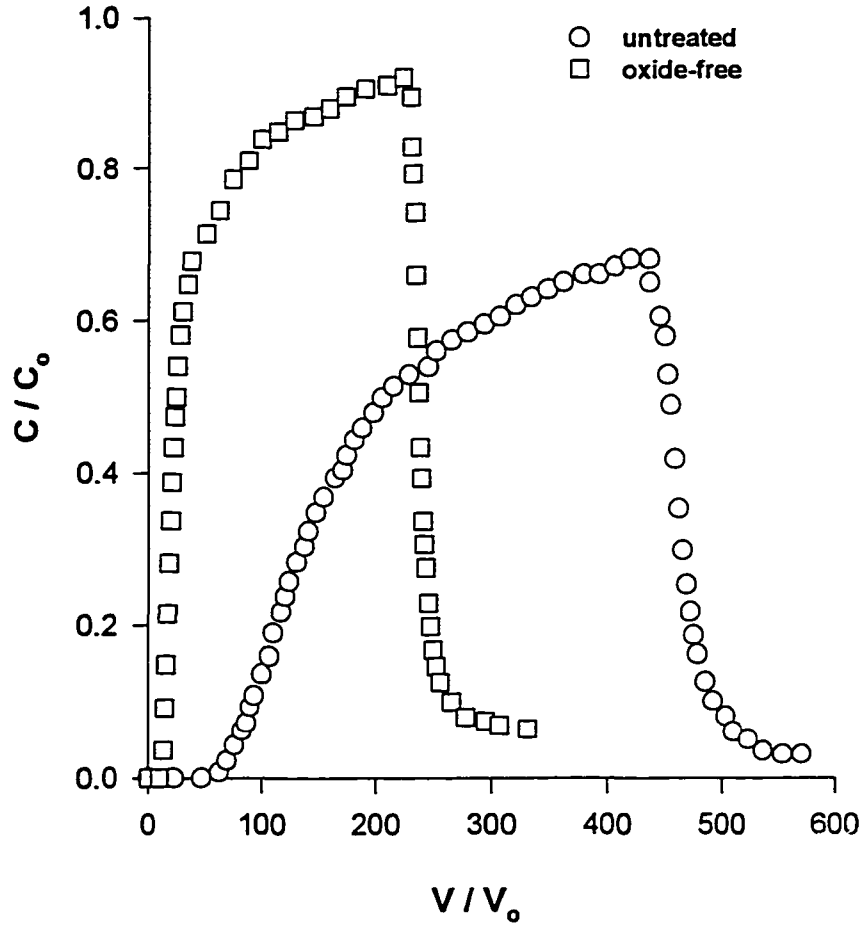


Fig. 3-11 The BTCs of Cu (II) in the packed aquifer columns

Cu was strongly sorbed by the solid phase, up to about 70 pore volumes. At this point, the column had adsorbed 106 μg Cu g^{-1} of aquifer material. Thus, approximately 20% of the adsorbing sites, which were presumably the most strongly sorbing sites, were saturated and more Cu could then be transported through the column. The Cu BTC of the untreated aquifer material was characterized by slowly increasing effluent Cu concentration. Up to a pore volume of 430, where the influent was terminated, the effluent Cu concentration increased to 70% of its influent concentration and tended to continuously increase. Since the quantity of Cu adsorbed increased with increasing solution Cu concentration (non-linear Langmuir adsorption isotherm, Fig. 3-4), the Cu adsorption and transport processes occurred simultaneously, giving rise to a broad slope of the BTC in the aquifer column. After the Cu input was terminated, the adsorbed Cu was desorbed with neutral salt (0.025 M $KClO_4$). The Cu concentration in the effluent declined rapidly, indicating that adsorbed Cu had limited tendency to be desorbed. The irreversibility of Cu adsorption is important in terms of reducing Cu mobility and preventing ground water contamination.

The Cu breakthrough in the oxide-free aquifer material (treated with dithionite) exhibited a very different behavior from that in the untreated aquifer material (Fig. 3-11). In the oxide-free aquifer column, Cu breakthrough occurred at a pore volume of approximately 15, with a steep initial slope. The retardation factor observed graphically for the Cu BTC was 24, whereas that for the Cu BTC in untreated column was as high as 200, i.e., 8 times higher than that in the oxide-free column. Thus, Fe and Mn oxides or hydroxides possessed dramatic potential to inhibit Cu mobility in the aquifer matrix. This observation is consistent with that from the batch adsorption experiment (Fig. 3-4).

Influence of DOC on Cu transport in the original aquifer medium

Influence of EDTA on Cu transport. For a better understanding of the influence of DOC on Cu transport, the co-transport of Cu and a defined ligand, EDTA, was investigated by the same procedure as the DOC / Cu transport studies that are described later on. The molar ratio of Cu to EDTA was 1:3 in the input solution. Since Cu and EDTA form a 1:1 chelate, it is assumed that all the Cu ions were essentially present in chelated form. The transport of chelated Cu in the aquifer material behaved like conservative tracers such as Cl^-, showing no interaction with the solid phase with a retardation factor around 1 (Fig. 3-12). Although metal (II)- EDTA complexes (e.g., NiEDTA, CaEDTA, CoEDTA, and PbEDTA) have been reported in the literature to be adsorbed by various Fe and Al oxides (Nowack et al., 1996), no CuEDTA adsorption by the aquifer material was observed in the present study. The implication of the observed Cu BTC in presence of EDTA is that organic ligands like EDTA can effectively compete with the solid phase for Cu ions and inhibit the adsorption of Cu ions by the solid phase. Through formation of a chelate, likely in neutral form, they act as a carrier responsible for a rapid transport of Cu through the aquifer medium.

The transport of EDTA itself was slightly retarded in the aquifer column compared with the EDTA-Cu complexes. At a pore volume of 2, the relative Cu concentration was 1.0, whereas the relative concentration of EDTA was 0.75 and reached 1.0 after approximately 50 pore volumes passed. Since the pH in the aquifer column was around 6.7 (lower than the PZC of the aquifer material), the solid phase was expected to carry a positive charge. The EDTA molecules which were not involved in chelation were mainly in divalent $EDTA^{2-}$ form. The interaction between $EDTA^{2-}$ and positively charged sites on the solid phase might explain the observed retardation. The adsorption of EDTA by Mn and Al

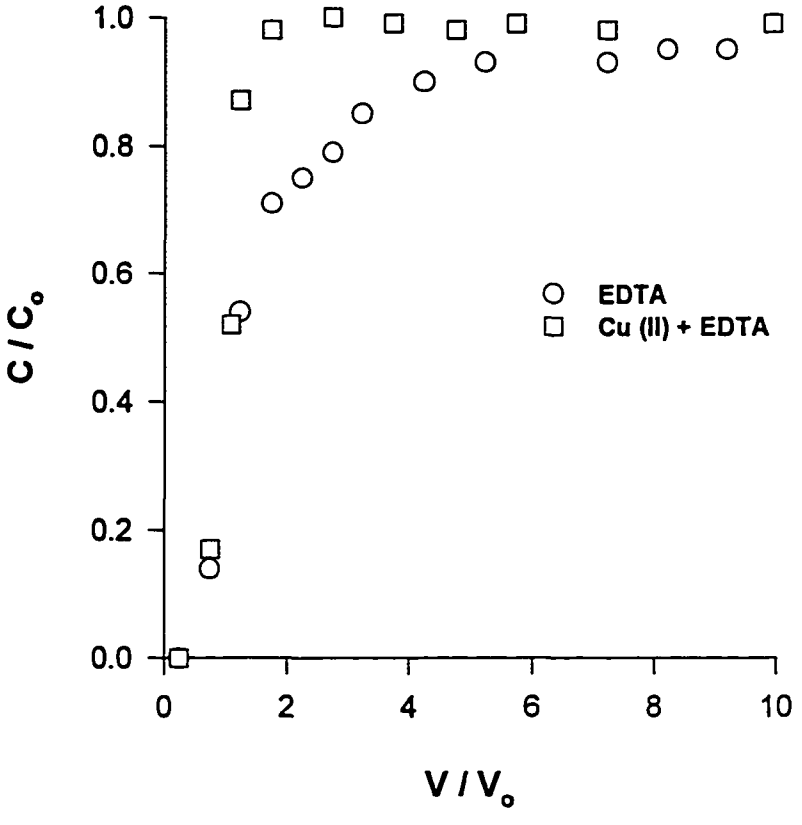


Fig. 3-12 The BTCs of EDTA and Cu (II)

(in the presence of EDTA) in the aquifer material

oxides was also reported by Blesa et al.(1984) and Bowers and Huang (1985). Bowers and Huang (1985) demonstrated that in addition to electrostatic attraction, specific ligand exchange can play a significant role in EDTA adsorption by an Al oxide.

Influence of molecular weight of the DOC on Cu transport. The organic substances in sludge-derived DOC varied in molecular weight, content of functional groups, and possibly structure as well. Thus, the influence of the DOC on Cu mobility is expected to be complex as compared to well-defined organic ligands. Fig. 3-13 presents the Cu BTCs in the presence of DOC with two different MW fractions. Up to 75 pore volumes, Cu was transported more readily in the presence of low MW DOC (MW500-3500 daltons) than without DOC presence. However, a retardation effect on Cu mobility was observed at a higher relative pore volume. The initial facilitation of Cu transport by low-MW DOC was expected since these compounds had high Cu-binding capacity (Fig. 2-2) and mobility (Fig. 3-6). But in terms of reactivity with Cu (II) and the solid phase, this MW fraction apparently consisted of at least two groups of organic compounds . It is hypothesized that one group of compounds could chelate Cu (II) effectively, resulting in low-charge or neutral species. These species, behaving like the Cu-EDTA chelate, could be transported rapidly through the aquifer column (Fig. 3-12). This group of compounds was not dominant in quantity because it resulted in C / C_o values of only about 0.1 by the 75th pore volume. But it was important in that some Cu^{2+} ions became more mobile in the presence of these compounds. The rest of the compounds in this fraction, dominant in quantity, seemed to favor Cu adsorption processes by the solid phase. Therefore, the dominant effect of this MW fraction on Cu mobility at the later stage of transport was retardation.

Mass balance calculations for Cu adsorbed and transported up to 150 pore volumes

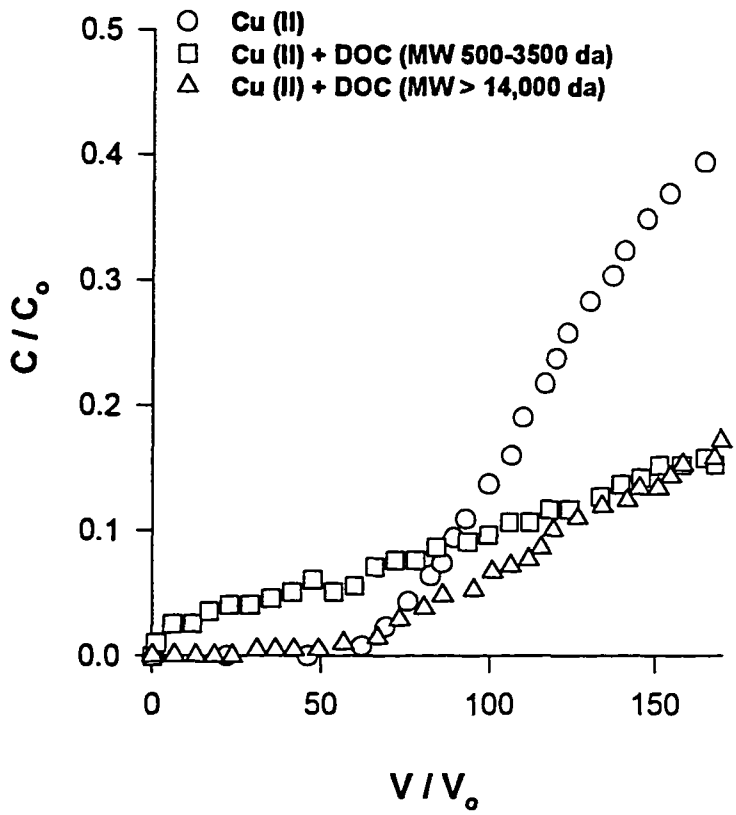


Fig. 3-13 The BTCs of Cu in the presence of DOC with different MWs in the packed aquifer columns

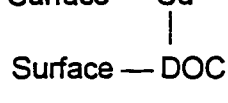
suggested that the quantity of Cu retarded by the aquifer column in the presence of the low-MW DOC fraction was 1.24 times greater than that in absence of any DOC. The presence of high-MW DOC (MW > 14,000 daltons) did not influence Cu transport up to 75 relative pore volumes and again retarded the Cu mobility significantly at a higher relative pore volume. The observed retardation effect was 1.34 times higher than in the DOC-free aquifer column within 150 pore volumes.

The retardation effect observed at higher pore volumes for both MW fractions was due to the increased Cu adsorption by the aquifer columns. The increase in metal adsorption by various clays, particularly oxides and hydroxides in the presence of DOC, have been reported extensively (Tipping et al., 1983; Davis, 1984; Davies-Colley et al., 1984; Oden et al., 1993; Zachara et al., 1994). The increase in metal adsorption by Fe and Al oxides promoted by various types of DOC was also observed to be enhanced as system pH increased below pH 7.5 (Murphy and Zachara, 1995). However, no universal explanation on the adsorption mechanisms is agreed upon.

Enhanced Cu adsorption by the mineral phase in the presence of DOC is often believed due to formation of ternary complexes among charged mineral surfaces, Cu cations, and the DOC ligands. A ternary complex may be formed in one of three patterns through covalent bonds (Davis and Leckie, 1979; and McBride, 1994):

i) Surface — Cu — DOC

ii) Surface — DOC — Cu

iii)


The hydroxyl groups of the oxides or hydroxides and various functional groups of the DOC are mainly responsible for the formation of ternary complexes. The ternary complexes so formed have been shown to have higher stability than chemisorbed Cu on the oxide surfaces (Davis, 1984). In the current study, the presence of DOC in the eluent enhanced Cu adsorption by the solid phase (Fig. 3-13), and the presence of Cu also increased the DOC adsorption by the material (Fig. 3-14 and Fig. 3-15). This synergism indicates that ternary complex formation was involved in the system. Cu (II) bridging between DOC and negatively charged aluminosilicate clays might also have occurred.

In a study on Co (II) adsorption by subsurface mineral materials in the presence of humic acids, Zachara et al.(1994) found that adsorption of humic acids by the solid phase consumed few metal-complexing sites on the humic substances or hydroxyl sites on the mineral surfaces. They believed that humic acid coating formed an open, highly porous structure on the surface which allowed the ready penetration of Cu ions to the sorbing sites of the oxides beneath. The total Cu adsorption was determined by the mineral surfaces and by the coated humic acids in an additive way. The additive mechanism might play a role in Cu adsorption by the aquifer column in the presence of DOC with MW > 14,000 daltons, however, current data did not allow distinction between this mechanism and others. According to the additive theory, low-MW fulvic acids are unlikely to enhance metal ion sorption by a solid phase since they are less likely to sorb to mineral surfaces (Zachara et al., 1994). The observed increased Cu adsorption by the aquifer phase in the presence of low-MW DOC (MW500-3500 daltons) (Fig. 3-13) suggests that the additive mechanism played a very limited role in the system.

In experiments studying the adsorption of Cu by humic substance-coated goethite, Tipping et al. (1983) observed that the goethite-HS particles had more high-affinity uptake

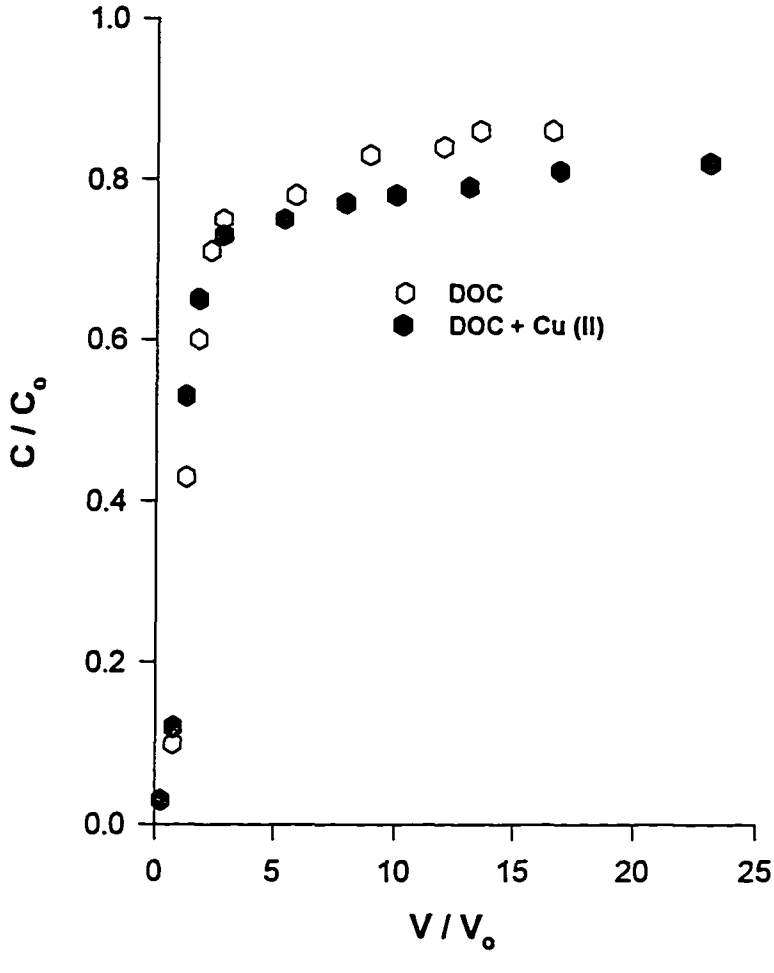


Fig. 3-14 The BTCs of DOC with MW 500-3500 daltons in packed aquifer columns

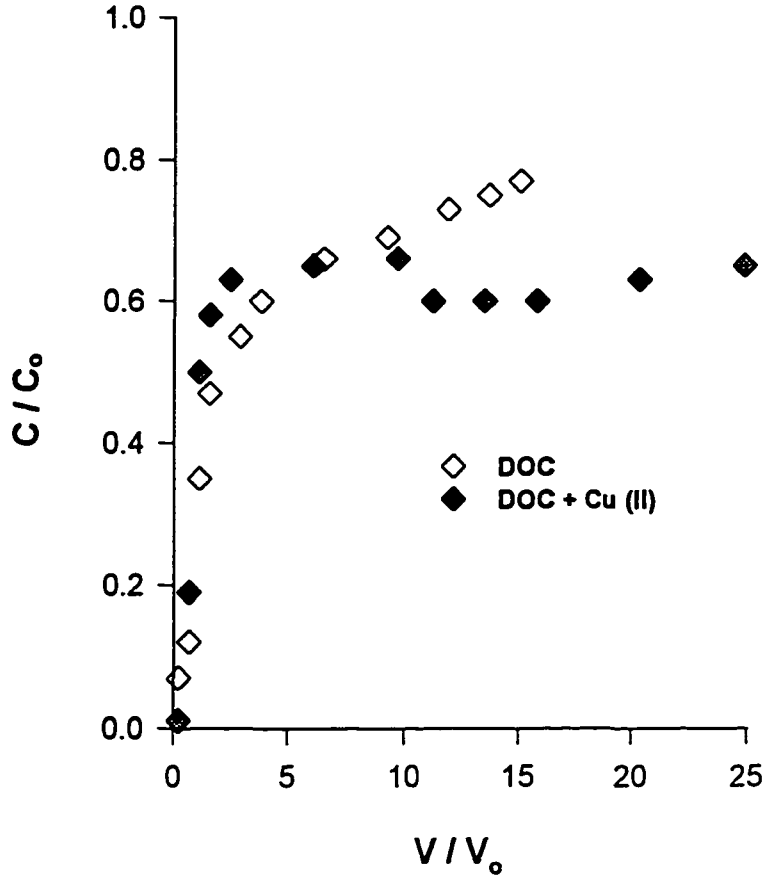


Fig. 3-15 The BTCs of DOC with MW > 14,000 daltons in packed aquifer columns

sites for Cu than did the goethite and humic substances acting independently, and they believed that the extra high-affinity sites could arise from electrostatic effects. In the absence of humic substances, goethite particles would carry a positive charge at pH 5.5. Copper ions would tend to be expelled from the surface of the particles through electrostatic repulsion. With humic substances in the system, on the other hand, adsorption of the humic substances by goethite particles renders them negatively charged. Thus, Cu^{2+} ions would then have a tendency to accumulate in the diffuse layer of the coated oxide surfaces. In the current study, a similar electrostatic effect might occur in the systems, since Fe and Mn oxides or hydroxides were the active components in the solid phase and the system pHs were adjusted to be lower than the PZC of the aquifer material. However, the extent of the electrostatic effect is unknown.

The mechanisms of increased Cu adsorption in presence of DOC are more complicated than our present understanding, and more research is needed in the future. The observed retardation effect of the DOC on Cu transport indicates that DOC may have a great potential to inhibit metal mobility in the aquifer medium. Many researchers believe that DOC may act as a carrier for metal movement through soils or aquifer media (e.g. Dunnivant et al., 1992a and McCarthy et al., 1993), and it may play a significant role in accumulation of metals in ground water. The present study suggests that the influence of DOC on metal transport is more complicated than what we would expect.

Influence of DOC with different polarity on Cu transport. The DOC subcomponents with different hydrophilicity / hydrophobicity characteristics might affect Cu transport differently due to their Cu-binding abilities and mobilities in the aquifer matrix. Breakthrough curves for Cu transport in the presence of hydrophilic DOC and hydrophobic acids with MW 500-3500 daltons are presented in Fig. 3-16 for the untreated aquifer

material and in Fig. 3-17 for the oxide-free material. The most distinguishing features between the two DOC subcomponents were that the hydrophilic DOC possessed less tendency to be adsorbed by the aquifer solid (Fig. 3-7) as well as a higher Cu-binding capacity (Fig. 2-3). With the same C to Cu ratio in the eluent, 59% of the Cu was in a complexed form for the hydrophilic DOC and 42% for the hydrophobic acid subcomponents. The hydrophilic DOC was expected to have a greater potential than hydrophobic acids to facilitate Cu transport in the aquifer column because of its higher mobility and metal binding capacity. The actual Cu breakthrough curves presented in Fig. 3-16 showed a general retardation of Cu transport in presence of both of the DOC subcomponents, although an initial period of enhanced transport was observed up to 75 pore volumes. This finding was consistent with the observation presented in Fig. 3-13. Up to 300 pore volumes, the hydrophilic DOC and hydrophobic acids exhibited a similar ability to retard Cu migration in the untreated aquifer medium (Fig. 3-16). At greater pore volumes, however, the hydrophilic subcomponent showed a larger tendency to inhibit Cu transport, and this phenomenon was more pronounced in the oxide-free matrix, probably because the high Cu-adsorbing capacity of oxides in the untreated material masked the difference between the two subcomponents in their influences on Cu mobility (Fig. 3-16). These results suggest that ternary complex formation between Cu-DOC complexes and oxide surfaces or Cu (II) bridging of the DOC to aluminosilicate clay surfaces was significantly involved in Cu retardation since the hydrophilic DOC (with higher Cu-binding ability) showed a greater potential to increase Cu adsorption. Oden et al. (1993) also reported that a complex formed between Cu (II) and soil- (or river-) humic substances was more adsorable by α - Al_2O_3 than Cu (II) alone, presumably due to ternary complex formation.

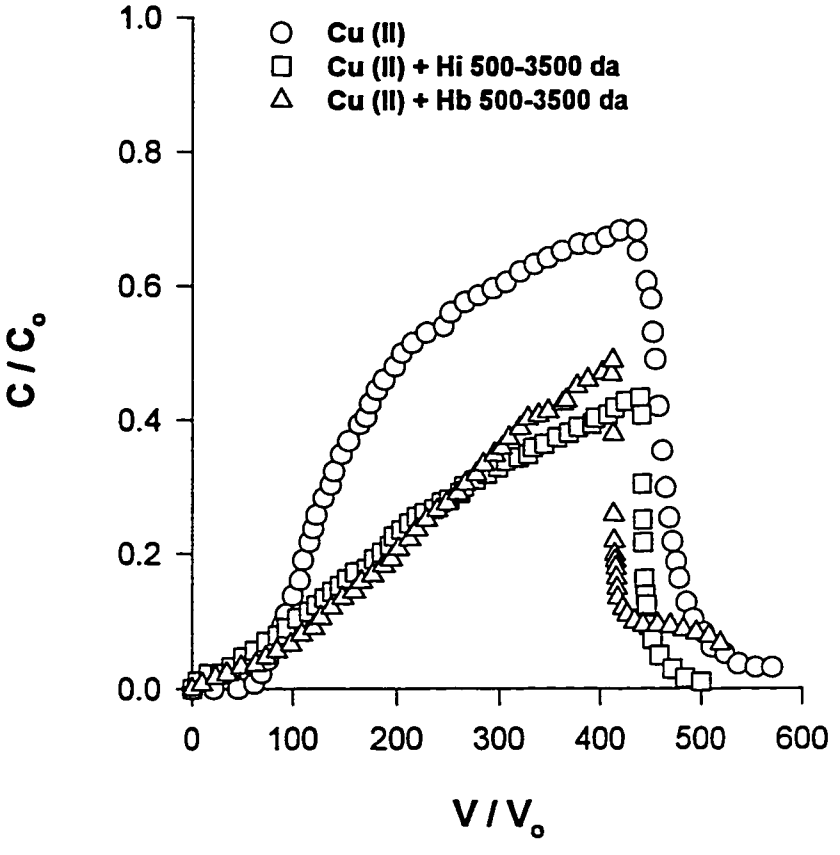


Fig. 3-16 The BTCs of Cu in the presence of DOC with MW 500-3500 daltons in packed columns

Hi = hydrophilic DOC, and Hb = hydrophobic acids

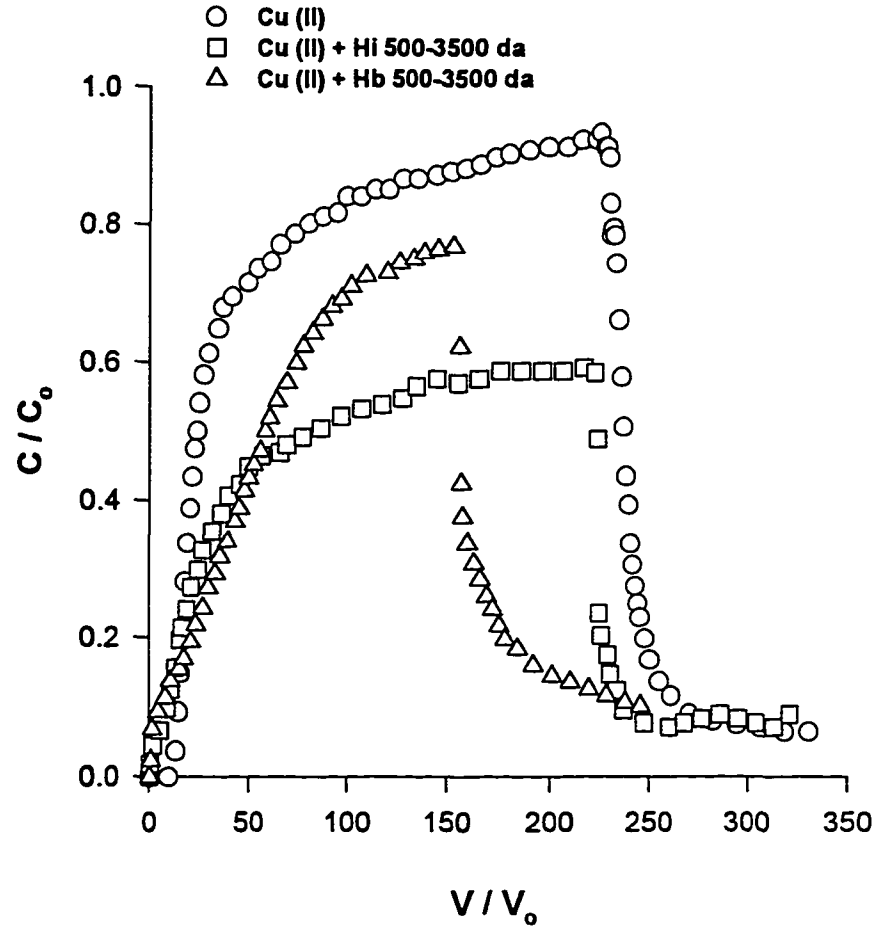


Fig. 3-17 The BTCs of Cu in the presence of DOC with MW 500-3500 daltons in oxide-removal material

Hi = hydrophilic DOC, and Hb = hydrophobic acids

Figure 3-18 presents the Cu BTCs in the presence of hydrophilic compounds and hydrophobic acids with MW > 14,000 daltons. The most striking difference between the two fractions was that the hydrophobic acid subcomponent possessed a higher Cu-binding capacity (Fig. 2-5) as well as a stronger tendency to be adsorbed by the aquifer phase (Fig. 3-8). Both DOC subcomponents inhibited Cu transport, although the hydrophilic subcomponent had a greater tendency to retard Cu migration. However, the retardation mechanisms between the two subcomponents are expected to be somewhat different from one another and different from low-MW DOC, as well. Unlike low MW-DOC, the hydrophilic subcomponent with MW > 14,000 daltons showed a very limited Cu-binding capacity, and less than 2% of the total Cu in the input solution was present in complexed form. Thus, ternary complex formation among the surface, Cu cations and organic ligands was expected to play minor role in the retardation of Cu transport. Although the exact mechanisms are not known, two factors are likely to have been involved in Cu uptake by the aquifer material in the presence of high-MW, hydrophilic DOC:

pH buffering. Since Cu was mainly present as free Cu^{2+} ions in the Cu / DOC input solution, the Cu uptake by the solid phase, to a large extent, occurred through chemisorption by the surface hydroxyl groups of Fe and Mn oxides or hydroxides. For example (Davis, 1984; McBride, 1994):

$$> Fe\text{-}OH + Cu^{2+} + H_2O \rightarrow > Fe\text{-}O\text{-}Cu\text{-}OH + 2\,H^{+}$$

The consequence of chemisorption of one Cu^{2+} ion onto a hydroxide or oxide surface is the release of two protons. During the sorption reaction, if the protons released were buffered by the dissolved organic compounds, the reaction was thermodynamically shifted more toward the right side of the equation and thus Cu sorption was favored. Fig. 3-19 shows evidence indicating the pH buffering effect of the dissolved organics. The pH of the

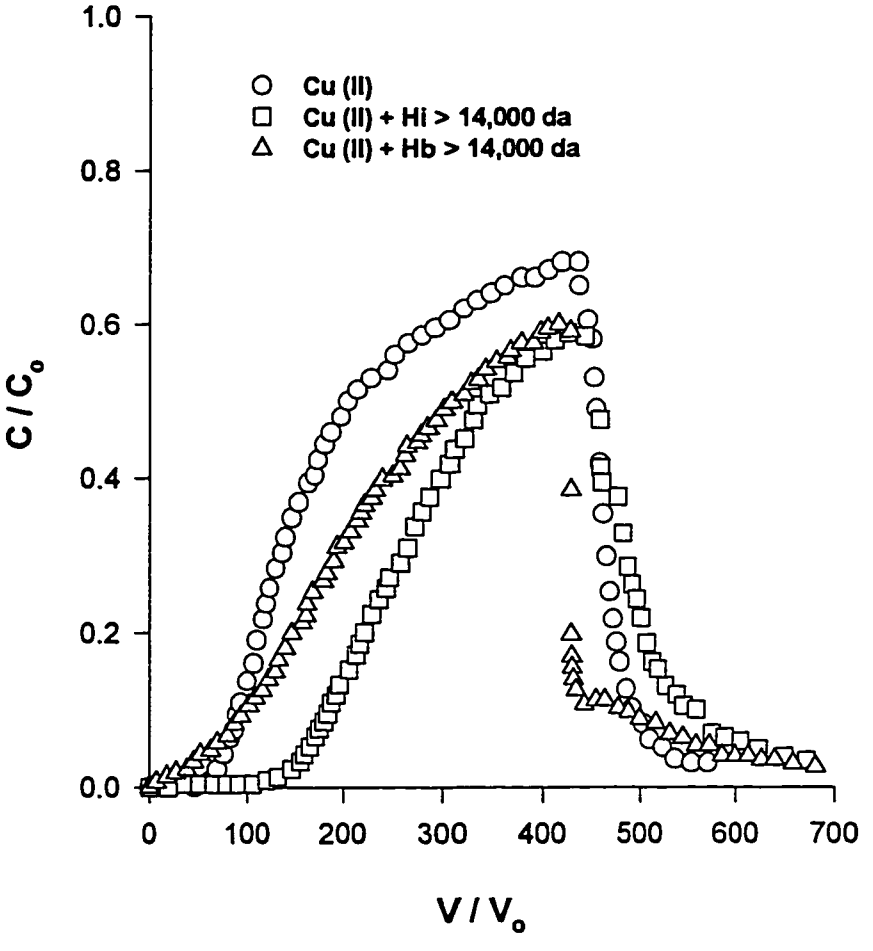


Fig. 3-18 The Cu BTCs in the presence of DOC with MW > 14,000 daltons in packed columns

Hi = hydrophilic DOC, and Hb = hydrophobic acids

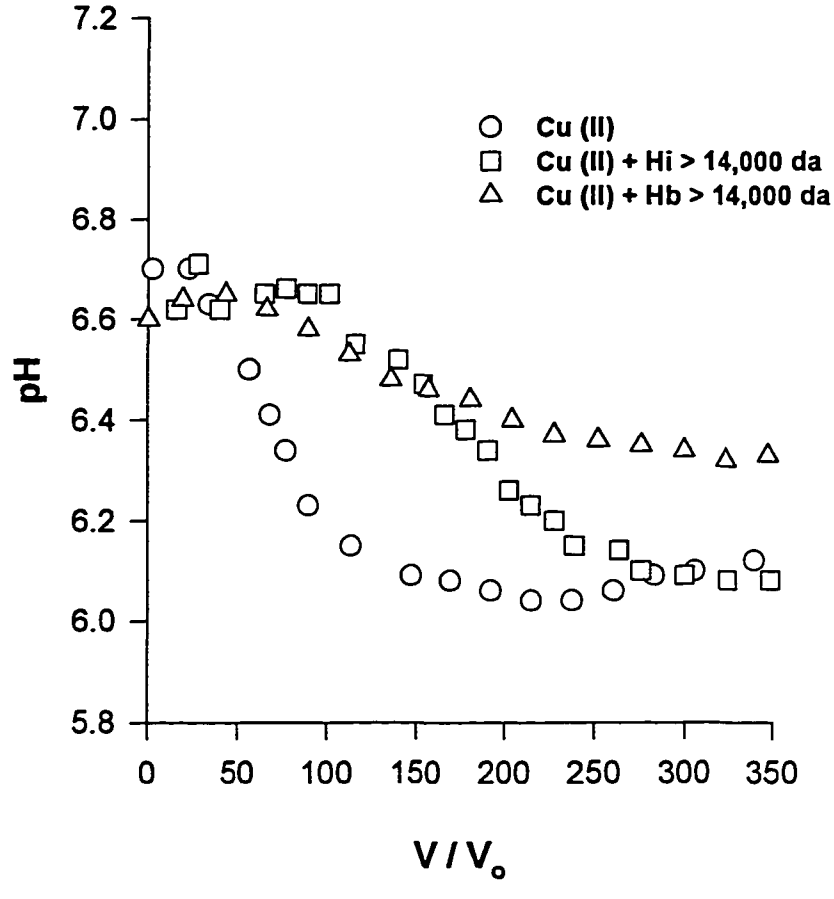


Fig. 3-19 The change in effluent pH in the presence of DOC with MW > 14,000 daltons

effluent in the DOC-free column decreased markedly from 6.6 to 6.1 in the first 100 pore volumes, whereas the effluent pHs in the presence of the hydrophilic subcomponent were decreased slightly within the same pore volume, coinciding with more retention of Cu by the solid phase (Fig. 3-18). However, this mechanism does not completely explain the retardation of Cu transport by the hydrophilic DOC subcomponent because the pH in the effluent decreased, although more gradually, to the same values as in the DOC-free column by 250 pore volumes. Also, the hydrophilic DOC subcomponent showed a more pronounced effect on Cu retardation than the hydrophobic acid subcomponent, although both subcomponents had a pH buffering effect (Fig. 3-18 and Fig. 3-19). Therefore, other factors may also be responsible for the observed phenomenon.

Electrostatic effect. Due to its low Cu-binding capacity, it is believed that the hydrophilic subcomponent (>14,000 da) was rich in neutral polymers like polysaccharides. The adsorption of large polymers on the solid surface would modify the properties of the diffuse double layer (DDL) of the solid phase. Consider the following hypothetical situation: Since the pH of the aquifer column was lower than the PZC of the material, the solid phase carried a net positive charge. In the absence of large-MW DOC, a portion of Cu cations was likely to experience electrostatic repulsion, being expelled by the surface and transported to the bottom of the aquifer column. However, adsorption of large neutral, organic polymers onto the surface caused by hydrophobic interaction would lower the electrokinetic potential in the DDL from ψ_d (diffuse double layer potential) to ζ (electrokinetic potential) due to displacement of the shear plane (Stumm and Morgan, 1981) (Fig. 3-20). The potential decrease across the DDL would reduce repulsion between the surface and Cu cations and probably create an environment for Cu cation accumulation in the diffuse layer. Tipping et al. (1983) pointed out that a change in the diffuse layer

potential of only 30 mV, which is similar to the change which adsorbing humic substances bring about, would produce a change in the electrostatic free energy of attraction of ca. - 6 KJ mol^{-1} for a divalent ion like Cu^{2+}. Indirect evidence supporting this hypothesis is the desorption curves shown in Fig. 3-18. The Cu adsorbed by the solid phase in the presence

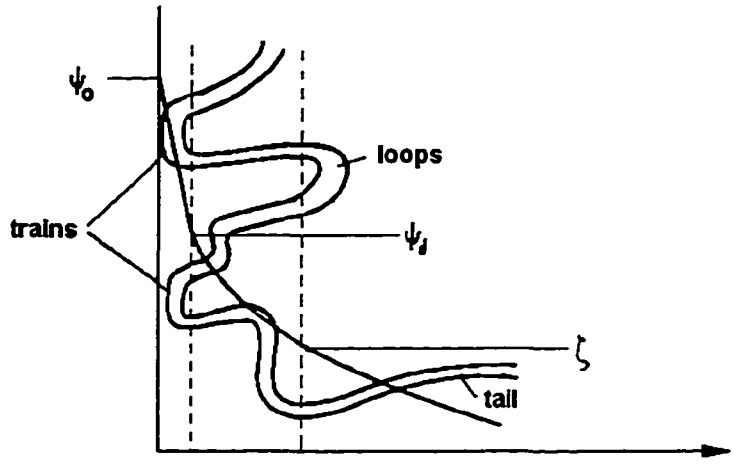


Fig. 3-20 Effect of adsorbed polymer on the double layer
(Stumm and Morgan, 1981)

of hydrophilic DOC exhibited a greater tendency to be desorbed compared to the DOC-free column. This suggests the presence of weakly adsorbed Cu on the surface.

The hydrophobic subcomponent with MW > 14,000 daltons had a greater Cu-binding capacity than the hydrophilic DOC and was capable of participating in ternary complex formation. Compared to the DOC-free column or the aquifer column in the presence of hydrophilic DOC, the Cu sorbed by the solid phase was less likely to be desorbed, suggesting that ternary complex formation was probably involved in Cu retardation and that the electrostatic effect was probably less important. It should also be

noted that this DOC subcomponent was able to transport some complexed Cu through the aquifer medium. This was suggested by an initial Cu breakthrough from the aquifer column (Fig. 3-18).

Comparison of Cu transport in the presence of hydrophilic or hydrophobic DOC with different MWs. For a better comparison of the influences of hydrophilic or hydrophobic DOC with different molecular weights on Cu mobility, the data presented in Fig. 3-16 and Fig. 3-18 were replotted and presented in Fig. 3-21 for the hydrophilic DOC and in Fig. 3-22 for the hydrophobic acids with two different molecular weights. The mass of Cu transported or adsorbed at selected pore volumes (arbitrarily chosen) in these columns was also calculated and presented in Table 3-2. Except for the hydrophilic DOC with MW > 14,000 daltons, the presence of various DOC compounds in the system apparently enhanced Cu mobility initially. At a pore volume of 75, the percentage of Cu transported in the presence of low-MW hydrophilic DOC (500-3500 daltons) was 7 times greater than that in the DOC-free system. Compared with the DOC-free column, about 5 times the amount of Cu was transported when hydrophobic acids were present (regardless of their molecular weights) within the first 75 pore volumes (Table 3-2). It should be pointed out that the observed enhanced transport may be more relevant to the field context than the DOC retardation effect discussed previously. Due to strict governmental regulation of land-applied sludge, sludge-borne Cu is typically present only in trace amounts. The sludge-derived DOC is more likely to facilitate first breakthrough of Cu, since the retardation effect apparently occurred only after high Cu input to the system.

For pore volumes between 75 and 400, all four DOC subcomponents inhibited Cu mobility compared with the DOC-free system. Apparently, the ability of these DOC subcomponents to retard Cu movement followed the order of (Table 3-2):

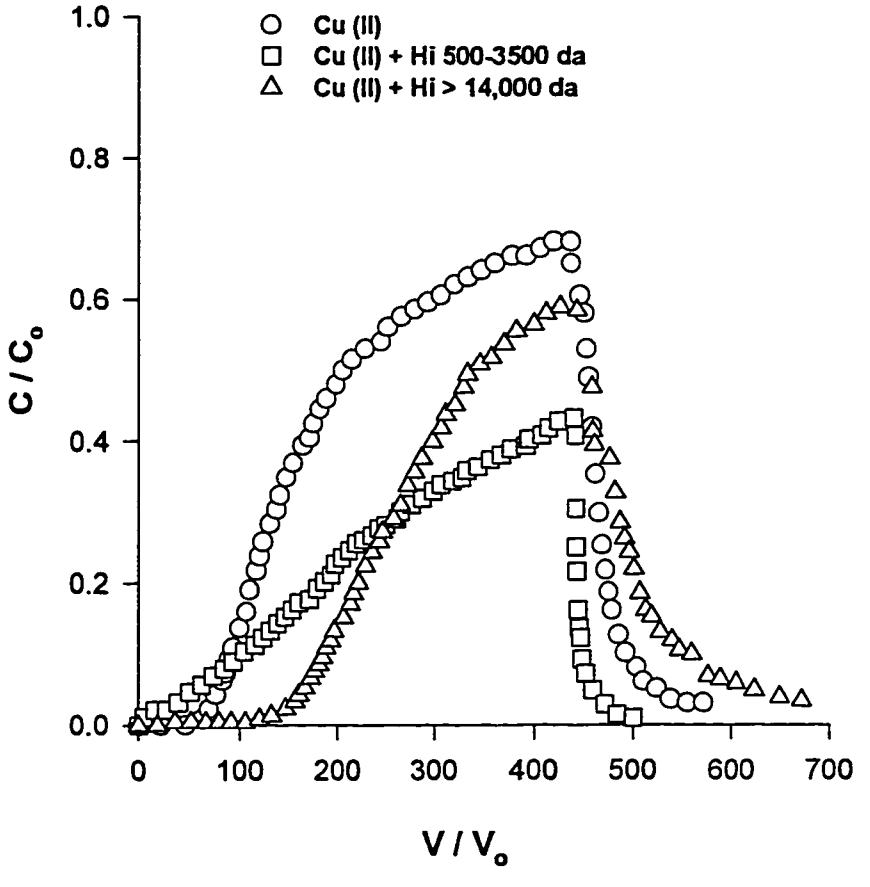


Fig. 3-21 The Cu BTCs in the presence of hydrophilic (Hi) DOC

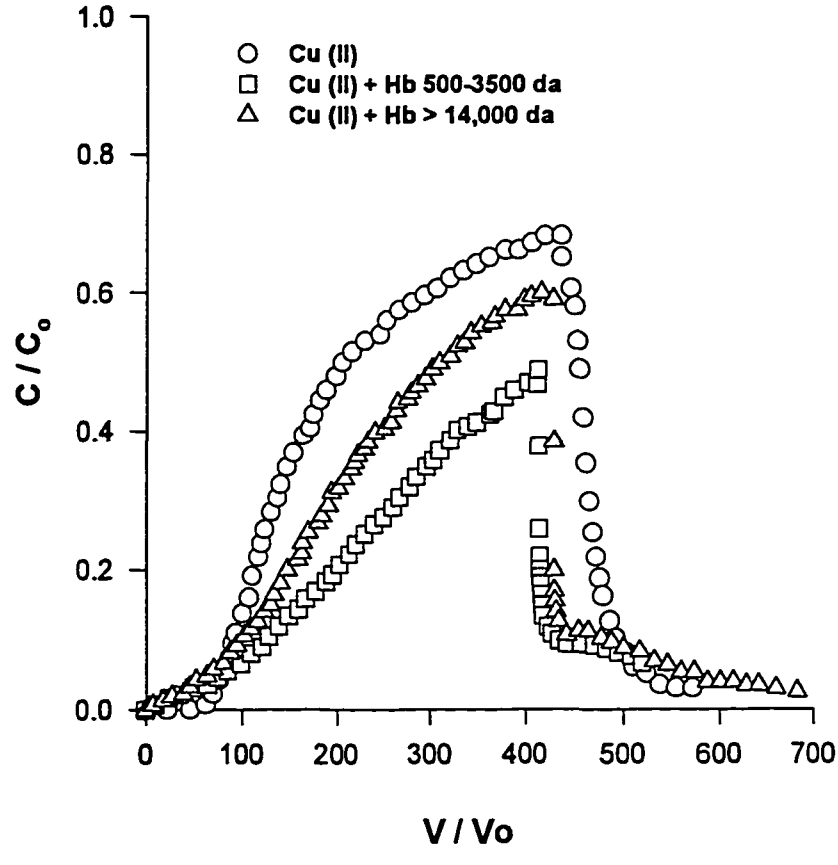


Fig. 3-22 The Cu BTCs in the presence of hydrophobic acids (Hb)

Hi (>14,000) > Hi (500-3500) > Hb (500-3500) > Hb (>14,000)

Cu retardation by hydrophilic DOC with MW > 14,000 daltons was mainly due to the delay in Cu breakthrough, and Cu was transported in the column readily in the later stages of the experiment. After the cross-over point in Fig. 3-21, low-MW hydrophilic DOC (500-3500 daltons) retarded Cu transport more strongly than the high-MW hydrophilic DOC. This is seen more obviously in Fig. 3-23 in the oxide-free material discussed in the next section. Similarly, low-MW hydrophobic acids inhibited Cu migration more strongly than high-MW hydrophobic acids (Fig. 3-22 and Table 3-2). The conclusion drawn from these observations is that the effect of DOC on Cu mobility is more dependent upon its functional group contents than its inherent mobility in the aquifer medium. Despite the high mobility, low molecular weight DOC is rich in various functional groups (Table 2-2) and may be actively involved in surface reactions like ternary complex formation. Consequently, it can retard Cu mobility significantly.

Table 3-2. The Cu (II) transported or adsorbed at chosen pore volumes

	Percentage of Cu transported (%) at V/V_o 75	Cu adsorbed (μg Cu /g material) between V/V_o 75 and 400
Cu (II)	0.5	245
Cu (II) + Hi 500-3500 da	3.6	376
Cu (II) + Hb 500-3500 da	2.6	361
Cu (II) + Hb > 14,000 da	2.9	314
Cu (II) + Hi > 14,000 da	0.3	387

V. Influence of sesquioxides on Cu transport in the presence of DOC

Since Fe and Mn oxides and hydroxides were the most abundant solid-phase components to react with Cu, the removal of the sesquioxides was expected to diminish the retardation of Cu transport in the aquifer columns, regardless of DOC effects. This was confirmed by the Cu BTCs in oxide-free aquifer columns in the presence of various DOC subcomponents, shown in Fig. 3-23 for hydrophilic DOC with different molecular weights and in Fig. 3-24 for MW 500-3500 fraction with different polarities. Despite the presence of various DOC subcomponents, Cu BTCs in the oxide-free material showed a rapid breakthrough within 30 pore volumes, while those in the untreated material presented a only slow breakthrough after 75 pore volumes. Thus, Fe and Mn oxides or hydroxide had a significant effect over DOC in controlling Cu mobility in the aquifer material.

The passage of various DOC subcomponents in oxide-free aquifer columns also indicated retardation of Cu transport, and the retardation trends were similar to those observed in untreated aquifer material. That is, the higher the functional group contents in the DOC subcomponents, the stronger the tendency for Cu to be immobilized in the oxide-free material. However, the degree of retardation was less than that found in untreated aquifer material. For a better comparison, the Cu concentration ratios at a relative pore volume of 150 were arbitrarily chosen and are listed in Table 3-3 for various experimental treatments. At this particular pore volume, in the absence of any DOC, the relative Cu concentration in effluent in the oxide-free aquifer column was 2.5 times higher than that in the untreated aquifer column. But the C / C_o of Cu in the oxide-free aquifer column in the presence of hydrophobic acids with MW 500-3500 daltons was 5.8 times higher than that in the untreated aquifer column in the presence of the same DOC subcomponent. This is also true for Cu transport in the presence of other DOC subcomponents. The results

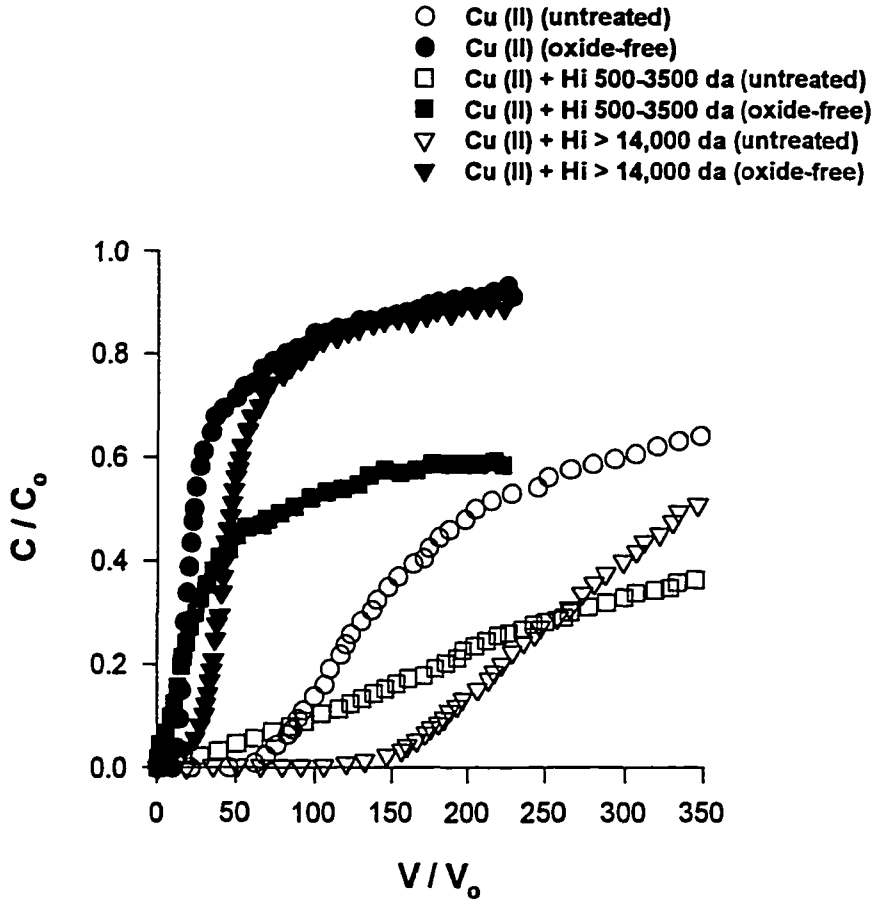


Fig. 3-23 The Cu BTCs in untreated and oxide-free aquifer material in the presence of hydrophilic DOC

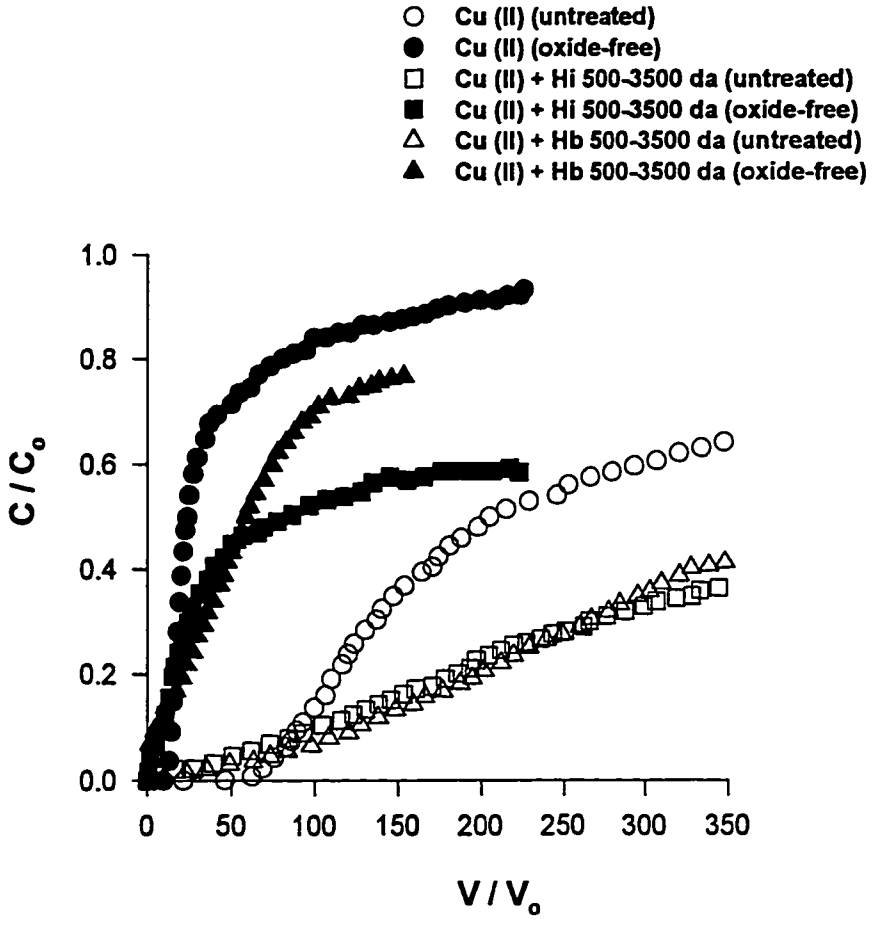


Fig. 3-24 The Cu BTCs in untreated and oxide-free aquifer material in the presence of DOC with MW 500-3500 daltons

Table 3-3 The Cu relative concentrations at a relative pore volume of 150

Aquifer column	Input solution	C / C_o	Relative conc. ratio (oxide-removed / untreated)
untreated	Cu (II)	0.35	
oxide-free	Cu (II)	0.87	2.5
untreated	Cu (II) + Hi > 14,000 da	0.30	
oxide-free	Cu (II) + Hi > 14,000 da	0.86	2.8
untreated	Cu (II) + Hi 500-3500 da	0.16	
oxide-free	Cu (II) + Hi 500-3500 da	0.57	3.5
untreated	Cu (II) + Hb 500-3500 da	0.13	
oxide-free	Cu (II) + Hb 500-3500 da	0.76	5.8

indicated that after removal of Fe and Mn oxides, the interactions among the DOC, Cu and the solid surface were reduced significantly, and more Cu could be transported through the aquifer material

CONCLUSIONS

The mobilities and their influences on Cu transport of various DOC subcomponents derived from a sewage sludge source were investigated in a sandy aquifer material by using laboratory columns. The main findings are summarized as follows:

The mobility of the dissolved organic substances in the aquifer material depended upon their molecular weights, polarity, and the composition of the aquifer material, etc. The low-MW DOC (MW 500-3500 daltons) had a higher mobility than the high-MW DOC (MW > 14,000 daltons). In terms of polarity, the mobility of the different subcomponents followed the order of hydrophilic DOC > hydrophobic acid > hydrophobic neutral. Similar observations were also reported by Dunnivant et al. (1992a) and McCarthy et al. (1993). These results indicate that large MW, more hydrophobic DOC has a stronger tendency to be adsorbed by the sandy aquifer, perhaps through hydrophobic interaction.

The studied DOC subcomponents varied in mobility and Cu-binding capacity (see detailed discussion in Part II), which might imply a potential difference among various DOC subcomponents in terms of their influences on heavy metal transport. The Cu BTCs in untreated aquifer columns (Fig. 3-16 and Fig. 3-17) revealed that low-MW DOC (MW 500-3500 daltons), regardless of polarity, enhanced Cu transport within the first 75 pore volumes, compared with the DOC-free experiments, and that, of the high-MW DOC fractions (MW > 14,000 daltons), only the hydrophobic acid subcomponent showed an initial effect of facilitating Cu transport. The hydrophilic DOC with MW > 14,000 daltons had a very limited Cu-binding capacity (Table 2-2), although it was more mobile than the hydrophobic acid DOC with the same molecular weight (Fig. 3-8). Thus the Cu-binding

ability of DOC played a more important role than the mobility of DOC in the facilitation of metal movement.

Of the three DOC subcomponents which enhanced Cu movement, the hydrophilic DOC with MW 500-3500 daltons had the greatest potential to mobilize Cu, probably due to having the highest Cu-binding ability among the three subcomponents. The amount of Cu transported in the presence of this subcomponent was approximately seven times higher than that in the DOC-free system. Both the low-MW and high-MW hydrophobic acid subcomponents had a similar ability to mobilize Cu, and, within the first 75 pore volumes, the quantity of Cu transported in the presence of the two DOC subcomponents was approximately five times higher than that in the DOC-free column. The enhancement of Cu mobility by the DOC subcomponents was attributed to the ability of a small fraction of compounds to form low-charge or neutral chelates which had limited interaction with the solid phase and were transported rapidly through the columns. These results suggest that sludge-derived DOC can mobilize metal ions like Cu, although it occurs only to a certain extent.

The later stages of the Cu BTCs (V/Vo > 75) in Fig. 3-16 and Fig. 3-18 clearly indicate a retardation effect of various DOC subcomponents on Cu mobility. The observed retardation effect was more closely related to their Cu-binding capacity than to their mobility. The richer the content of functional groups, the stronger the retardation effect was. The presence of DOC in the aquifer columns enhanced Cu adsorption by the solid phase, while the presence of Cu also increased the DOC adsorption by the material (Fig. 3-14 and Fig. 3-15). These observations suggested that ternary complex formation between oxide surfaces and DOC-Cu complexes participated in the Cu retardation. The bridging of Cu (II) between DOC and negatively charged silicate clay surfaces might be

involved as well. The observed retardation effect has significant environmental implications. Under heavy land application of municipal sewage sludge, even though sludge-derived DOC and heavy metals might reach shallow aquifers through preferential flow paths, the increased metal adsorption by the aquifer matrix in the presence of DOC would reduce the overall release of these metals to groundwater and alleviate the possible groundwater contamination.

The Fe and Mn oxides and hydroxides in the studied aquifer material played an extremely important role in reducing Cu mobility through the chemisorption of Cu and the formation of ternary complexes. The retardation effect of the oxides on Cu mobility significantly surpassed that of any DOC subcomponent.

GENERAL CONCLUSIONS

Land application of sewage sludge may introduce certain harmful trace metals into agricultural soils and cause surface and ground water contamination. The dissolved organic carbon (DOC) in sludge has a potential to influence the migration of metals in soils and aquifers because of its metal-binding ability and mobility. The major objective of the present study was to characterize the DOC in a digested sewage sludge and a sludge-amended soil and to examine the influence of various sludge-derived DOC subcomponents on Cu mobility in an aquifer material, which was collected 230 cm below the surface near the sludge application field.

Dissolved organic carbon from the digested sewage sludge was separated into three molecular weight (MW) fractions, MW 500-3500 daltons, MW 3500-1400 daltons and MW > 14,000 daltons. DOC in each fraction was further fractionated into hydrophilic DOC, hydrophobic acids and hydrophobic neutrals by an XAD-8 chromatography technique. The Cu-binding abilities of these subcomponents were investigated by using a Cu ion-selective electrode technique. Their mobilities and influences on Cu transport in the sandy aquifer material were examined with column experiments. The effect of sludge application on soil extractable DOC content and composition was also evaluated under two types of vegetation.

Land application of sludge significantly increased the amount of extractable DOC in the soil and shifted the MW distribution of extractable soil DOC to the lower weight fraction (<14,000 daltons). Similar to sludge-derived DOC, the extractable DOC in the amended soil was richer in hydrophilic subcomponents than in hydrophobic subcomponents.

As the DOC increased in molecular weight, the Cu-binding capacity decreased significantly, indicating that low-molecular weight DOC had more metal-binding sites

compared with high-molecular weight DOC. For the DOC with MW 500-3500 daltons, the hydrophilic subcomponent presented a greater Cu-binding capacity than the hydrophobic DOC, while the hydrophobic acid subcomponents were the most important components in Cu-binding for higher-molecular weight DOC (MW > 3500 daltons). The maximum Cu-binding capacities of the DOC subcomponents ranged from 1.85 to 14.30 mmol Cu mol^{-1} DOC.

The low-MW DOC (MW 500-3500 daltons) was found to be highly mobile, whereas the high-MW DOC (MW >14,000 daltons) had a greater tendency to be adsorbed by the solid phase. Within the same MW fraction, the mobility of DOC followed the order of hydrophilic DOC > hydrophobic acids > hydrophobic neutrals. Cu breakthrough curves in the presence of the DOC subcomponents showed that, except for the hydrophilic DOC with MW > 14,000 daltons, all other DOC subcomponents enhanced Cu transport through the aquifer columns at relatively early stages of transport. At the later stages, all the DOC subcomponents significantly inhibited Cu mobility. The facilitation or retardation effect of various DOC subcomponents on Cu mobility was closely related to their Cu-binding abilities rather than to their mobilities.

Many investigators have believed that highly mobile, hydrophilic DOC could act as a carrier for metal ion transport in soil and aquifer matrix. The important finding of the current study is that the DOC in sludge can mobilize Cu to a certain extent but also inhibit Cu mobility dramatically when a significant amount of Cu is present in the system. Ternary complex formation among Cu, DOC and oxide surfaces is believed to be involved in the inhibition. Retardation of Cu mobility in the presence of DOC would reduce the potential of metal release to groundwater, alleviating concerns about possible ground-water contamination where sewage sludge is applied.

APPENDIX I RAW DATA OF DOC FRACTIONATION IN THE SLUDGE-AMENDED SOIL

Raw data of DOC fractionation in the sludge-amended soil

		Treatment (Mg ha^{-1})	Colloidial C	Total DOC	MW < 14,000 da	MW < 14,000 da (Hi)	MW < 14,000 da (Hb)	MW < 14,000 da (Hn)	MW > 14,000 da	MW > 14,000 da (Hi)	MW > 14,000 da (Hb)	MW > 14,000 da (Hn)
							μg C g^{-1} soil					
Switchgrass grass	rep I	42 (0-5 cm)	12.41	59.16	39.27	20.83	1.67	16.77	19.89	15.83	0.95	3.11
		42 (5-25 cm)	75.33	35.99	24.18	10.74	1.13	12.31	11.81	5.70	0.65	5.46
		22 (0-5 cm)	27.22	65.15	40.58	23.88	1.79	14.91	24.57	15.00	1.16	8.41
		22 (5-25 cm)	112.0	24.38	10.57	6.65	0.45	3.47	13.81	8.44	0.54	4.83
		0 (0-5 cm)	93.69	30.95	13.63	7.95	0.60	5.08	17.32	12.32	0.65	4.35
		0 (5-25 cm)	124.5	21.03	6.75	4.05	0.38	2.32	14.28	11.43	0.49	2.36
	rep II	42 (0-5 cm)	42.15	167.76	111.1	72.05	4.99	34.10	56.62	43.58	1.21	11.83
		42 (5-25 cm)	33.02	40.49	28.39	20.73	0.72	6.94	12.10	10.23	0.25	1.62
		22 (0-5 cm)	29.96	66.29	37.03	28.30	1.34	7.39	29.26	23.23	0.70	5.33
		22 (5-25 cm)	111.8	26.20	13.84	10.53	0.45	2.86	12.36	10.07	0.31	1.98
		0 (0-5 cm)	89.64	27.02	14.83	11.85	0.40	2.58	12.19	8.97	0.44	2.78
		0 (5-25 cm)	134.0	18.22	8.65	7.51	0.28	0.86	9.57	8.11	0.35	1.11
Poplar tree	rep I	42 (0-5 cm)	53.30	68.15	48.44	27.96	2.09	18.39	19.71	12.97	0.88	5.86
		42 (5-25 cm)	125.0	30.35	16.12	9.71	0.68	5.73	14.23	8.83	0.67	4.73
		22 (0-5 cm)	94.22	33.66	15.01	8.67	0.65	5.69	18.65	11.09	0.85	6.71
		22 (5-25 cm)	123.4	20.45	8.06	5.21	0.32	2.53	12.39	8.17	0.50	3.72
		0 (0-5 cm)	65.51	32.84	15.98	12.19	0.53	3.26	16.86	10.48	0.72	5.66
		0 (5-25 cm)	125.5	21.10	8.80	6.23	0.35	2.22	12.30	8.21	0.50	3.59
	rep II	42 (0-5 cm)	44.20	55.96	33.31	20.02	1.38	11.91	22.65	15.30	0.93	6.42
		42 (5-25 cm)	172.1	34.61	16.90	11.34	0.68	4.88	17.71	12.01	0.69	5.01
		22 (0-5 cm)	60.19	47.78	27.29	15.45	0.92	10.92	20.49	13.24	0.95	6.30
		22 (5-25 cm)	119.8	22.34	10.83	8.01	0.46	2.36	11.51	8.13	0.46	2.92
		0 (0-5 cm)	113.9	27.46	16.50	12.96	0.43	3.11	10.96	8.34	0.43	2.19
		0 (5-25 cm)	124.9	19.50	11.64	9.29	0.35	2.00	7.86	6.13	0.27	1.46

APPENDIX II THE FREE Cu BTCs IN THE PRESENCE OF VARIOUS DOC SUBCOMPONENTS IN UNTREATED AQUIFER COLUMNS

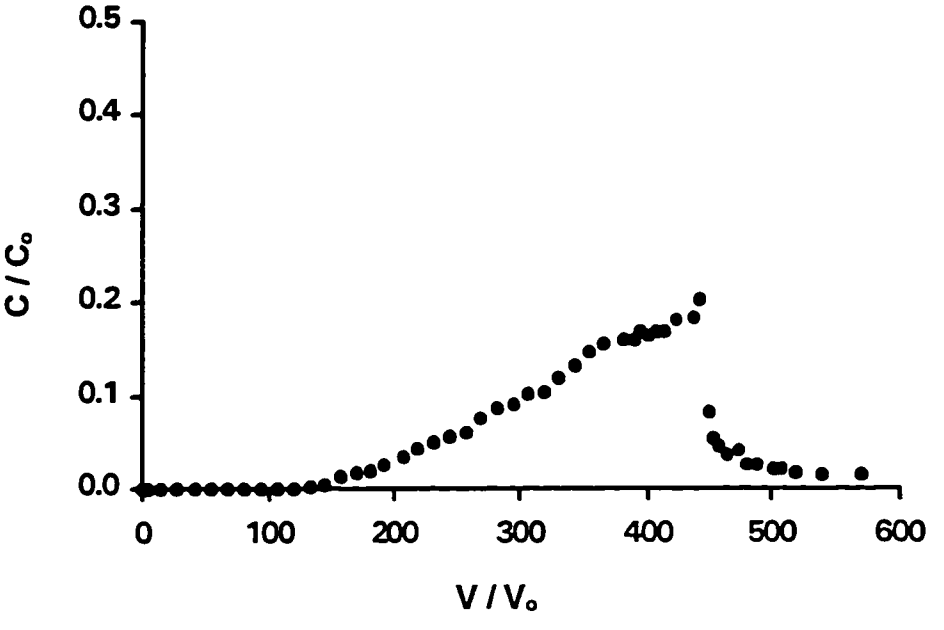


Fig. II-1 The Cu BTC in the presence of hydrophilic DOC with MW 500-3500 daltons

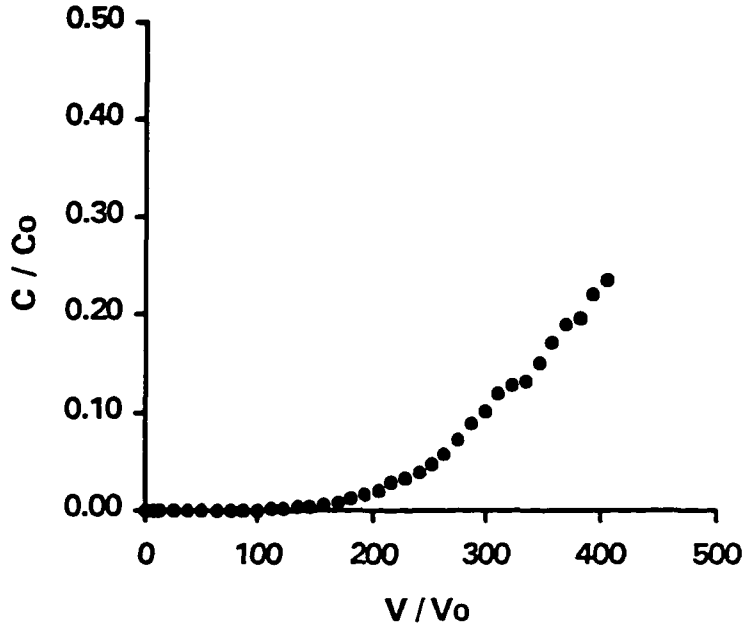


Fig. II-2 The free Cu BTC in the presence of hydrophobic acids with MW 500-3500 daltons

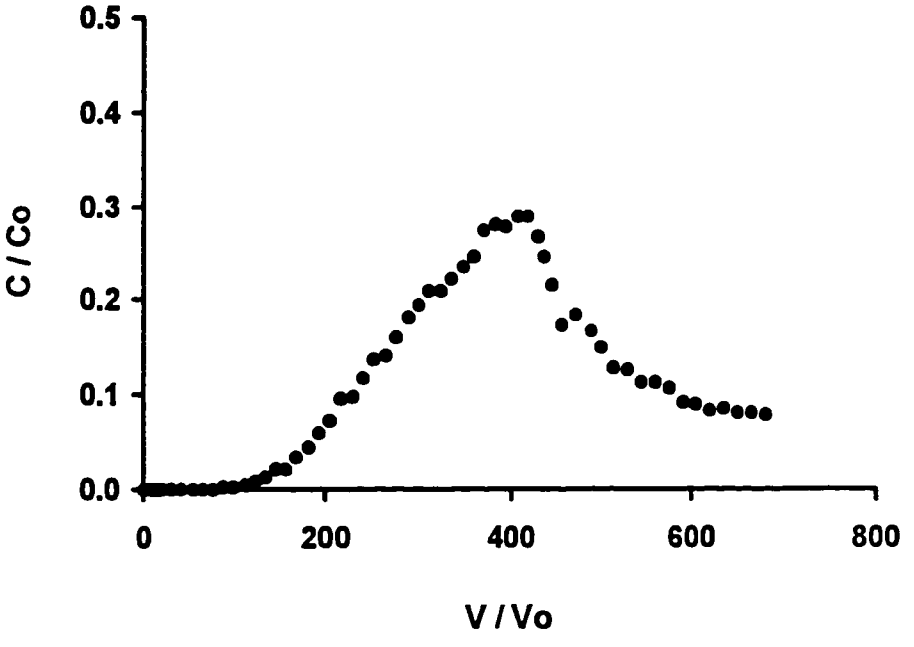


Fig. II-3 The Cu BTC in the presence of hydrophobic acids with MW > 14,000 daltons

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